Green Bay Urban Air Toxics Monitoring

A Summary Report for the Period July 1991 - June 1995

Author's Note

This report summarizes data collected during the first 4 years of Wisconsin's Urban Air Toxic Monitoring Program. Two different prototype sites were established in Green Bay during this time. Data is analyzed on the basis of program completeness, simple statistical analysis of results, temporal trends where applicable, and comparisons with other studies as available.

A memo prepared by Jeff Myers, Air Management staff toxicologist, is included as an addendum to the report to provide a review of this data from a toxicological standpoint.

At the current time, another year and a half worth of data has been collected, and many of the recommendations suggested in this report have been adapted. A summary report on the data from July 1995 through June 1996 should be available shortly after this report is. More comprehensive data analysis will be reported in the future, including wind direction/ parameter concentration correlations.

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Executive Summary

The Clean Air Act Amendments of 1990 define an approach to Hazardous Air Pollutants (HAPS) which includes seeking a substantial reduction in emissions and public health risks associated with exposures. As a part of this, a research program is outlined which includes ambient monitoring for a broad range of HAPs in a representative number of urban locations.

The Wisconsin Urban Air Toxics Monitoring Network (WUATM) was conceived in response to these directives. The full network was originally planned to consist of 4 or 5 monitoring stations located throughout the state. A single prototype site was established in Green Bay during 1991. Funding for additional sites has yet to be appropriated.

The initial monitoring was designed to be a screening program to determine concentrations of organic and inorganic compounds present in Wisconsin's urban air. The program is considered to be a screening program because only a limited number of compounds have been collected and quantified. Most of these compounds are listed in Table 1 below. In general, the compounds can be grouped as semi-volatile organic compounds (including polynuclear aromatic hydrocarbons, PCBs and pesticides), polar organic compounds (formaldehyde and phenols), volatile organic compounds and non-volatile metals.

The air toxics monitoring network is intended to provide information for the following uses:

- Determine concentrations of HAPs in Wisconsin's Urban Atmospheres
- Assess Potential Air Toxics Problems
- Background Data and Trend Analysis
- Fate of Air Toxics

The prototype site in Green Bay has the additional purpose of evaluating various sampling and analytical methodologies.

The initial monitoring site was established at Bay Beach in Green Bay in July 1991. The site remained here until March 1993, when the site was moved to a more centralized location along the Fox River. This report is intended to summarize results from the entire monitoring period through June 1995, and to make recommendations concerning the continuation and expansion of the toxics monitoring network. An addendum to the report evaluates the data presented in terms of the toxicological risks associated with

PAHs as a compound class are among the most studied of the air toxics. As such, results from around the world are available for comparison. Total determined PAH values throughout the

monitoring period ranged from 1.5 to 249.8 nanograms per cubic meter (ng/m^3) with an average of 22.5 ng/m^3. An average yearly total PAH value reported for Los Angeles is 10.9 ng/m^3.

Polychlorinated biphenyl (PCB) and pesticide samples were collected, with PCB values ranging from 0.282 ng/m^3 to 1.998 ng/m^3, with an average of 0.718 ng/m^3. These values appear somewhat lower than values reported from the EPA's Great Lakes National Program Office pilot atmospheric monitoring network at the University of Wisconsin, Green Bay Campus during 1989. That study reports levels of PCBs ranging from 3 ng/m^3 to 6.5 ng/m^3. Additionally, atrazine, dieldrin, hexachlorobenzene and lindane have all been detected in the ambient air in Green Bay.

Formaldehyde values in Green Bay range from 0.067 ug/m^3 (0.054 ppbv) to 57.1 ug/m^3 (46.5 ppbv), with an average of 2.62 ug/m^3 (2.14 ppbv). Formaldehyde is monitored elsewhere in the state as part of the Photochemical Assessment Monitoring (PAMS) program. Average values from Milwaukee are comparable to those from Green Bay, in addition to those from studies located in other states.

A variety of volatile organic compounds considered Toxics have been detected in the atmosphere of Green Bay. Detected values have ranged from 0.1 ppbv to 4.7 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene are less than 1 ppbv (average acetylene value is 2.47 ppbv). Where overlap exists between the PAMS and the Toxics VOC lists, comparisons between Milwaukee and Green Bay are possible and indicate generally similar concentrations of various parameters. Although VOC concentrations tend to be highly variable based on location, values obtained in other published air toxic studies are generally in the same order of magnitude as those found in Green Bay.

A suite of 6 metals (arsenic, cadmium, chromium, lead, selenium and vanadium) have been well characterized at the Green Bay sites. Average detected values are 1.766 ng/m^3, 0.550 ng/m^3, 4.037 ng/m^3, 12.506 ng/m^3, 2.065 ng/m^3, and 3.774 ng/m^3, respectively. These values are comparable to those obtained in other urban air toxic studies. An additional screening for the presence of other potentially hazardous metals present in Green Bay's air was performed with results presented in this report.

In summary, the toxics monitoring prototype site in Green Bay provides a significant quantity of information regarding a number of toxic compounds present in the air of this city. Trends over the 4 year period can be analyzed, and comparisons made with similar sampling from other locations. Ample opportunity has been available for the evaluation of methods used to collect and analyze trace components of the atmosphere.

Over the monitoring period to date, a number of method changes have been made to improve detection limits and consistency of results. Some of these changes include lengthening the PCB sampling period from 24 to 72 hours, changing the VOC collection technology from adsorbent tubes to passivated stainless steel canisters, and improving the analytical detection limits for PCBs and metals. Additional work remains to be done in improving the methods in use and expanding the toxics monitoring program.

Recommendations regarding continued operations and expansion of the toxics monitoring network fall into two basic categories: further refinements of methods, and expanding the network to different localities. Several of the methodology changes documented later in this report are already being implemented as this report nears completion.

The original intention of the program was to install permanent sites in 4 or 5 cities around the state. As it currently stands there is not funding available for such an ambitious expansion. However, there are ways in which toxics data from other locales can be generated without the large expense of installing new fixed site monitors. A combination of rotation of samples between other existing sites for TSP metals and remotely sampling for semi-volatile and volatile organic compounds using portable samplers would be an inexpensive way to help locate toxic hot spots and gather data from other parts of the state.

Table 1: Parameter List for Wisconsin Urban Air Toxics Monitoring Program

Benzo (a) Pyrene	Dioxins	Methylene Chloride
Chrysene	Furans	Chloroform
Fluoranthene	Hydrogen Sulfide	1,1,1-trichloroethane
Naphthalene	Phenols	Trichloroethene
Phenanthrene	Formaldehyde	Benzene
Total PCBs	Acetaldehyde	Toluene
Atrazine	Acetone	Xylene
Dieldrin	TSP	Styrene
DDT	Arsenic	1,4-dichlorobenzene
Hexachlorobenzene	Cadmium	Cumene
Lindane	Chromium	1,3-butadiene
Technical Chlordane	Lead	Tetrachloroethane
TCDD	Selenium	1,1,2,2-tetrachloroethane
TCDF	Vanadium	Carbon Tetrachloride

Sampling and Analytical Procedures

Sampling and analytical procedures for all parameters are specified in the Hazardous Air Contaminants Fixed Urban Site Monitoring Program Quality Assurance Project Plan (QA 8.0) prepared by DNR personnel in 1991. Specific methods are documented in the DNR Air Monitoring Handbook.

Semi-Volatile Organic Compounds: Polynuclear Aromatic Hydrocarbons (PAHs)

PAH samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and PUF plug, following EPA TO-13 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at a rate of approximately 8 cubic feet per minute (CFM) for a period of 24 hours. The sample is then packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis.

Analysis for these parameters is performed at the Wisconsin Occupational Health Laboratory (WOHL). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 3 mls. The sample is analyzed by high performance liquid chromatography (HPLC) with a fluorescence detector to determine the presence of selected PAH's.

Semi-Volatile Organic Compounds: Polychlorinated Biphenyls and Pesticides (PCBs)

PCB samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and PUF plug, following EPA TO-4 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at the maximum possible rate. This rate varies from slightly over 8 CFM to as much as 9.5 CFM, depending upon the condition of the sampler motor. The initial sampling protocol called for a 24 hour sampling period. This was changed in October 1993 to a 72 hour period because of a lack of results under the shorter sampling time.

Following collection of the sample, the filter and PUF plug are packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis. Analysis for these parameters is performed at the State Lab of Hygiene (SLOH). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 10 mls. The extracts are analyzed by gas chromatography with an electron capture detector to determine the presence of selected chlorinated compounds. Confirmation of compounds is through the routine use of dual column analysis, with occassional mass spectroscopy.

Semi-Volatile Organic Compounds: Dioxins and Furans

Dioxin samples were collected during 1992 from the Bay Beach site. Collection for the samples involved using a General Metal Works PS-1 sampler loaded with a combination quartz filter and PUF plug, following EPA TO-9 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at the maximum

possible rate. This rate varies from slightly over 8 CFM to as much as 10 CFM, depending upon the condition of the sampler motor. The sampling protocol called for a 72 hour sampling period. Three monthly samples were composited in the laboratory to generate a quarterly sample.

Following collection of the sample, the filter and PUF plug were packed in hexane rinsed aluminum foil and stored until shipment to the laboratory for analysis. Analysis for these parameters was performed at Enseco Incorporated in California. PUF plugs and filters were extracted with benzene, concentrated and then taken through a series of clean-up steps to remove interferences. The extracts were analyzed by high resolution gas chromatography with high resolution mass spectroscopy detection to determine the presence of chlorinated Dioxins and Furans.

Polar Organic Compounds: Carbonyls

Carbonyl samples are collected by drawing a known volume of ambient air through commercially prepared cartridges containing 2,4-dinitro phenylhydrazine (DNPH) coated silica gel, following EPA TO-11 as outlined in DNR OP 8.4, Aldehyde Sampling with 2,4-Dinitro phenylhydrazine impregnated sampling cartridges. Aldehydes react with the DNPH to form stable derivatives which can then be analyzed. Samples are collected over a 24 hour period at a rate of approximately 700 cc/min. Following collection, samples are refrigerated until shipment to the laboratory.

Aldehyde samples are analyzed at WOHL. The exposed cartridges are washed with acetonitrile to remove the aldehyde-DNPH derivatives. The eluant is brought to a known volume and then analyzed by reversed phase HPLC coupled with UV absorption detection.

Polar Organic Compounds: Hydrogen Sulfide

Hydrogen sulfide samples were collected between July 1991 and January 1994. The collection method followed the protocol adopted from NIOSH Method S4, involving an alkaline suspension of cadmium hydroxide. The method used is clarified in DNR OP.8.6, Sampling Polar Volatile Organic Compounds with Liquid Adsorbents. Aspiration of the sulfide containing air through the collecting solution results in the precipitation of cadmium sulfide, which can be subsequently determined by spectrophotometric methods. Sulfide samples were collected over 24 hours at a rate of approximately 700 cc/min.

Analysis of this parameter was performed at WOHL. The exposed solution is mixed with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride to produce methylene blue, which is then measured spectrophotometrically.

Polar Organic Compounds: Phenols

Phenols were sampled as part of the Wisconsin Urban Air Toxics Monitoring program between July 1991 and January 1994. Two different methods of collection were used during this period.

A liquid absorption procedure following EPA TO-8 protocols as outlined in DNR OP.8.6, Sampling Polar Volatile Organic Compounds with Liquid Adsorbents, was used initially, between July 1991 and August 1993. In this method, a known volume of ambient air was drawn through a solution of 0.1N NaOH. Samples were collected for a period of 24 hours at a rate of approximately 700 cc/min. Impinger samples were analyzed at WOHL using reverse phase HPLC coupled with fluorescence detection.

The second method, used between August 1993 and January 1994, used commercially prepared XAD-2 resin tubes as the collection medium. A known quantity of air was drawn through the tube at a rate of approximately 700 cc/min for 24 hours. Analysis involved solvent desorption of the tube followed by reverse phase HPLC coupled with fluorescence detection. Analysis was performed at WOHL.

Volatile Organic Compounds

Sampling and analysis of VOCs has also employed two different methods at the Green Bay toxic site. The first method, employed between July 1991 and September 1993, involved concentrating ambient VOCs on adsorbent tubes. The second method, initially adopted in July 1994 and continued through the present, uses whole air samples collected in passivated stainless steel tanks.

The adsorbent tube sampling technique involved drawing air through 4 sampling tubes attached in parallel to a manifold. The method is documented in DNR OP.8.7, Sampling Nonpolar Volatile Organic Compounds with Solid Adsorbents. The tubes used a Carbotrap^{TM} adsorbent. The distributed volume technique was used, where two samples would be collected at one volume, and two others at a volume four times the first. All four samples would be sent to the lab, with the two primary tubes (one at x volume, the other at 4x) analyzed by thermal desorption gas chromatography/mass spectroscopy, and the remaining two tubes held as backup samples in case problems were encountered during the analysis. This analysis was performed at WOHL.

The canister method follows the protocols of EPA TO-14 employing passivated stainless steel canisters. A low flow 24 hour sample is collected in an evacuated canister, which is then sent to the laboratory for cryogenic concentration followed by high resolution gas chromatography with mass spectroscopic detection. The analysis is performed at Biospheric Research Corporation in Hillsboro, Oregon.

Total Suspended Particulate and Metals

Standard high volume methods as documented in DNR OP.1.2, High Volume Sampler, are employed at the Green Bay Toxic monitoring sites for the collection of TSP samples. A 24 hour sample is collected on a pre-weighed glass fiber filter at an average flow rate of 1.42 m^3 per minute. Filters are sent to the SLOH for determination of total mass of particulate collected. The same sample is used for determination of ambient concentrations of non-volatile metals. The metals are determined by digesting a portion of the filter in acid and analyzing the resulting

solution using atomic absorption spectroscopy.

Quality Assurance Objectives

Several aspects of quality control and assurance protocols have been incorporated into the monitoring program in Green Bay. The quality assurance objectives are precision, accuracy, completeness, representativeness and comparability.

Precision for discrete samples is determined by means of quarterly duplicate samples. The goal is for the duplicates to be within +/- 15% for each individual parameter.

Accuracy is intended to be determined on two levels, that of sampling using air flow audits, and also analytical accuracy through submission of spiked samples. Sampler audits are performed yearly by personnel other than the regular site operator, with the goal being to have the actual flow rate within +/- 10% of the expected sampling air flow rate.

Analytical relative accuracy determinations are made by submitting samples spiked with representative compounds. These samples are occasionally available from EPA and other sources. Several of these samples were submitted. In addition, spiked media recovery determinations are a typical part of the analytical in-house quality control mechanism. The goal for accuracy determinations are for the results to be within +/-25% of the actual amount introduced to the media.

The completeness parameter involves trying to obtain valid samples for all scheduled sampling days. Monitoring plans call for sampling metals every 6 days. All other parameters were sampled on an off-set every 13 days schedule through early 1993, when all organic parameters began on an every 12 day schedule, which continues through this time.

Representativeness is accomplished through meeting the criteria for sampling locations set forth by USEPA in the Compendium of Methods for the Determination of Toxic Organic Compounds and 40 CFR Part 58, Appendix E. Comparability involves reporting data in units consistent with other organizations reporting similar data. In general, volatile compounds are reported in part per billion volume (ppbv), while semi-volatile and non-volatile compounds are reported in micrograms or nanograms per cubic meter (ug/m^3 or ng/m^3).

Results

Polynuclear Aromatic Hydrocarbons, Data Completeness

Records for collection of PAH samples begin in September 1991. Samples collected before November 12, 1991 were lost due to analytical recovery problems in the laboratory. No samples were collected between January 3, 1992 and April 16, 1992 while PUF plug background determinations were being made in the laboratory. In addition, samples were not collected between October 10, 1993 and October 11, 1994, in part because of a lack of PUF plug

availability.

Project completeness with reference to PAHs is documented in the following tables. Table 2 relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. It should be noted that the periods of non-sampling noted above are not subtracted out of the sampling days. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days.

Table 2: Polynuclear Aromatic Hydrocarbon Sampling Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Sampling Days
Overall	64.0%	84	71	8	5	111
1991	100.0%	9	8	1	0	8
1992	71.4%	23	20	1	2	28
1993	76.7%	26	23	2	1	30
1994	16.7%	7	5	2	0	30
1995	100.0%	19	15	2	2	15

Figure 1 on page 9 presents the data in Table 2 graphically. Table 3 documents analytical completeness in terms of results obtained for samples submitted. Reasons for analytical incompleteness may include loss of samples in the laboratory through poor recovery early in the program, and samples misplaced by the sample operator or in the mail system. Completeness in this table is the ratio of Samples to Samples Submitted.

Table 3: Polynuclear Aromatic Hydrocarbon Analytical Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Samples Submitted
Overall	90.5%	76	62	9	5	84
1991	44.4%	4	4	0	0	9
1992	108.7%	25	20	3	2	23
1993	100.0%	26	22	3	1	26
1994	42.9%	3	2	1	0	7
1995	94.7%	18	14	2	2	19

Results of all samples were evaluated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. Some 76 sets of results were reported by the laboratory out of a total of 84 samples collected. Table 4 below summarizes results for all PAH analytical parameters in terms of reporting of results. The column "Percent Detection" represents the ratio of Total Detects to Reported values. "Percent Completeness" represents the ratio of Reported to the total number of samples submitted (84).

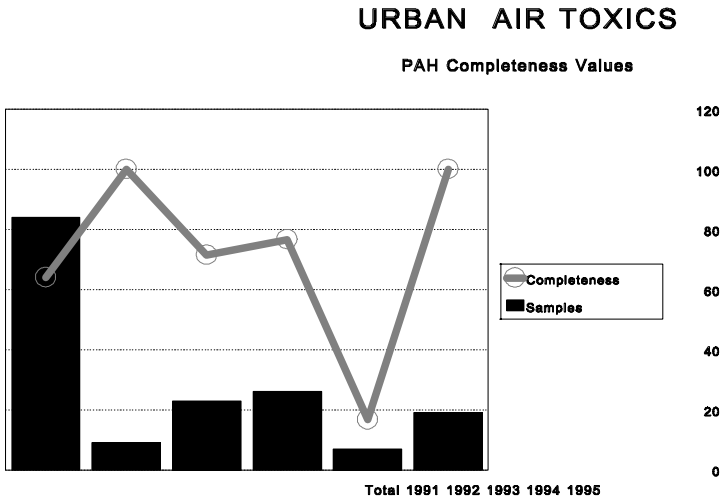

URBAN AIR TOXICS
PAH Completeness Values
120
100
80
60
40
20
0
Completeness
Samples
Total 1991 1992 1993 1994 1995

Table 4: Polynuclear Aromatic Hydrocarbon Detects

Analytical Parameters	Reported	Clean Detects	Interference	Total Detects	Percent Detection	Percent Completeness
BENZ (A) ANTHRACENE	7	0	0	0	0.0%	8.3%
BENZENE SOLUBLE ORGANICS	3	3	0	3	100.0%	3.6%
BENZO ALPHA PYRENE (BAP)	76	40	5	45	59.2%	90.5%
CHRYSENE	76	16	6	22	28.9%	90.5%
CORONENE	4	0	0	0	0.0%	4.8%
FLUORANTHENE	75	52	4	56	74.7%	89.3%
NAPHTHALENE	70	55	2	57	81.4%	83.3%
PHENANTHRENE	76	48	0	48	63.2%	90.5%
PYRENE	2	2	0	2	100.0%	2.4%

The table above represents parameters reported numerically by the laboratory. Figure 2 on page 9 represents data from this table graphically. Numerous other parameters have been mentioned in the lab reports without quantification. These parameters and the number of times the peaks have been mentioned are documented in table 5 below. It should be noted that the Total Mentions of a particular parameter do not necessarily represent the number of samples the parameter was present in.

Table 5: Other Polynuclear Parameters

Parameter Name	Total Mentions	Percent of Samples
Perylene	14	16.7%
Anthracene	11	13.1%
Pyrene	17	20.2%
B(a)Anthracene	15	17.9%
Coronene	14	16.7%
3-methyl Cholanthrene	10	11.9%

Polynuclear Aromatic Hydrocarbons, Analytical Results

Results were evaluated in a number of ways. The tables following represent summation on the basis of all samples, by site, by year and by season respectively. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. All

values are maximum possible values, as non-detects were evaluated at the detection limit.

Additional reporting criteria include the number of detects, whether or not the analytical parameter was detected in any blanks, and how many samples reported each particular parameter. Results are reported as ng/cubic meter.

Table 6: Polynuclear Hydrocarbon Results, Summary of All Samples (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank
BENZ(A)ANTHRACENE	1.068	4.006	0.008	128.9%	0	N
BENZO(A)PYRENE (BAP)	0.105	3.093	0.003	364.2%	39	Y
CHRYSENE	3.774	196.941	0.016	630.9%	14	N
CORONENE	0.259	0.458	0.143	46.0%	0	N/A
FLUORANTHENE	3.944	33.620	0.130	142.5%	51	Y
NAPHTHALENE	2.483	14.276	0.180	107.9%	52	Y
PHENANTHRENE	12.299	106.562	0.600	155.6%	47	Y
PYRENE	1.842	2.039	1.645	10.7%	2	N/A

Samples: 73 Blanks: 6 Duplicates: 5

Figure 3 on page 13 displays the data presented in table 6 for the five main polynuclear parameters.

Samples were collected from the Bay Beach site between July 1991 and March 1993, and at the Fox River site from April 1993 through the present. Enough data is present to evaluate the sites separately for determining if there is a significant difference between the two sites in terms of polynuclear aromatic compound concentrations. The most significant difference appears to be the phenanthrene results, with the Bay Beach site averaging 7.768 ng/m^3 , while the Fox River average is 16.696 ng/m^3 , in spite of the significantly higher maximum recorded at Bay Beach. This could be an indication of differentiation between the sources impacting each respective site, however our parameter list is not comprehensive enough to fingerprint the results for this type of determination.

The maximum values for benzo(a)pyrene, chrysene and fluoranthene were all obtained on a single day (12/21/91). The next highest values for these parameters are 0.671, 7.332, and 22.458 ng/m^3 respectively. The sample records for this period indicate that a week before the sampling date there was a fire in the area.

Evaluation of results when disregarding the episodic results of 12/21/91 from the Bay Beach

averages yields 0.039 +/- 112.8%, 1.184 +/- 137.8% and 2.909 +/- 115.6% ng/m^3 for benzo(a)pyrene, chrysene and fluoranthene respectively. The differences present between the fire affected results and the regular sampling clearly indicates not only the impact an event of this nature can have, but also the potential for this type of sampling to track and monitor combustion events. It is especially interesting to note that the elevated values were observed a week after the fire.

Table 7a: Polynuclear Aromatic Hydrocarbon Samples from Bay Beach (ng/m^3)

Parameter Name	Average	Maximum	Minimum	%RSD	Detects	In Blank?	Reported
BENZO (A) PYRENE	0.130	3.093	0.003	403.9%	23	N	35
CHRYSENE	7.175	196.941	0.518	468.1%	6	N	35
FLUORANTHENE	3.718	33.620	0.130	166.1%	27	Y	35
NAPHTHALENE	2.250	14.276	0.180	129.7%	22	Y	29
PHENANTHRENE	7.768	106.562	0.600	234.3%	20	N	35
PYRENE	1.842	2.039	1.645	10.7%	2	N/A	2

Samples: 35 Blanks: 2 Duplicates: 3

Table 7b: Polynuclear Aromatic Hydrocarbon Samples from Fox River (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE	1.068	4.006	0.008	128.9%	0	N	7
BENZO (A) PYRENE	0.081	0.671	0.008	171.8%	16	Y	38
CHRYSENE	0.473	2.436	0.016	98.7%	8	N	38
CORONENE	0.259	0.458	0.143	46.0%	0	N/A	4
FLUORANTHENE	4.177	22.458	0.134	119.0%	24	N	36
NAPHTHALENE	2.676	13.848	0.182	91.5%	30	Y	38
PHENANTHRENE	16.696	75.378	0.805	113.8%	27	Y	38

Samples: 38 Blanks: 4 Duplicates: 2

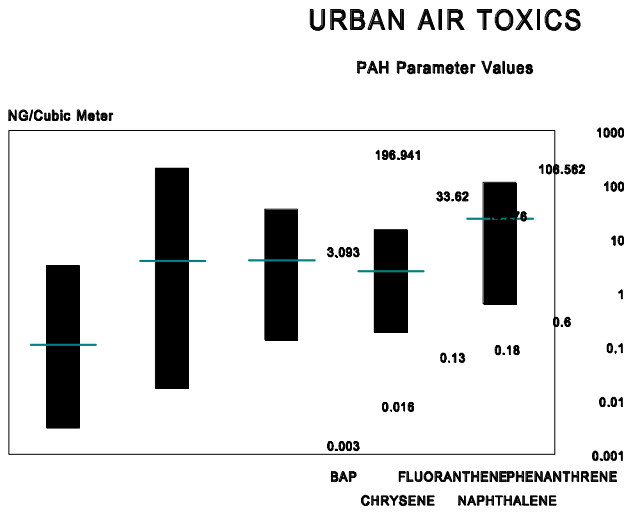
An effort to evaluate whether the polynuclear compound concentrations are changing as time goes on is displayed in the following tables, which show results by calendar year. It should be noted that 1991 and 1994 have only 4 and 3 samples respectively. This sparsity of samples in 1991 has led to skewed results when combined with the highest recorded values for three of the parameters. Results presented in table 8a through 8e are presented graphically in figure 4 on page 13.

Table 8a: Polynuclear Aromatic Hydrocarbon Results, 1991 Summary (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZO (A) PYRENE	0.876	3.093	0.082	146.3%	4	N/A	4

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
CHRYSENE	52.366	196.941	2.796	159.4%	4	N/A	4
FLUORANTHENE	9.809	33.620	1.645	140.2%	4	N/A	4
NAPHTHALENE	3.961	8.336	0.521	85.7%	4	N/A	4
PHENANTHRENE	9.528	15.385	4.578	44.0%	4	N/A	4
PYRENE	1.842	2.039	1.645	10.7%	2	N/A	2

Samples: 4 Blanks: 0 Duplicates: 0


URBAN AIR TOXICS
PAH Parameter Values
NG/Cubic Meter
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100
10
1
0.1
0.01
0.001
196.941
108.562
33.62
3.093
0.6
0.13
0.18
0.016
0.003
BAP
FLUORANTHENE
PHENANTHRENE
CHRYSENE
NAPHTHALENE

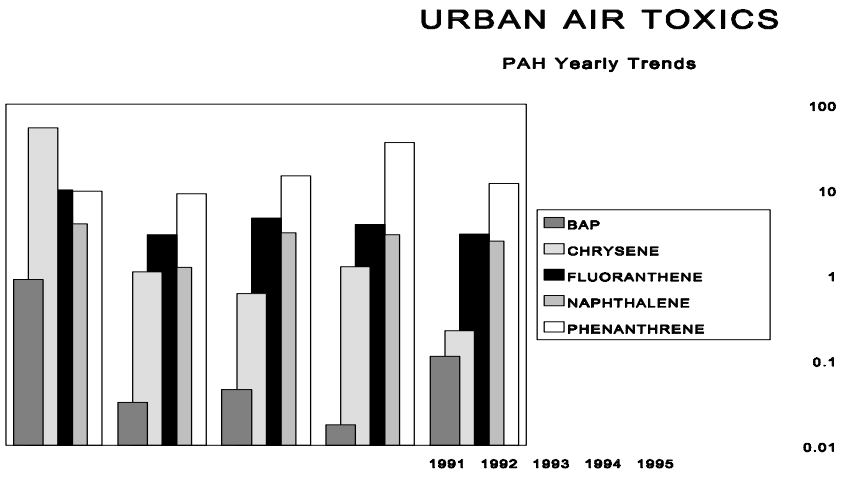

URBAN AIR TOXICS
PAH Yearly Trends
100
10
1
0.1
0.01
BAP
CHRYSENE
FLUORANTHENE
NAPHTHALENE
PHENANTHRENE
1991
1992
1993
1994
1995

Table 8b: Polynuclear Aromatic Hydrocarbon Results, 1992 Summary (ng/m³)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZO (A) PYRENE	0.032	0.102	0.003	90.5%	18	N	23
CHRYSENE	1.072	7.332	0.533	147.0%	2	N	23
FLUORANTHENE	2.947	13.040	0.133	117.0%	18	N	
NAPHTHALENE	1.220	2.459	0.180	49.6%	13	N/A	17
PHENANTHRENE	8.920	106.562	0.600	245.8%	14	N	23

Samples: 23 Blanks: 1 Duplicates: 2

Table 8c: Polynuclear Aromatic Hydrocarbon Results, 1993 Summary (ng/m³)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE	1.595	4.006	0.371	88.7%	0	N/A	4
BENZO (A) PYRENE	0.045	0.418	0.008	186.4%	9	Y	25
CHRYSENE	0.601	1.681	0.291	39.7%	1	N	25
CORONENE	0.259	0.458	0.143	46.0%	0	N/A	4
FLUORANTHENE	4.580	22.458	0.130	128.2%	14	Y	23
NAPHTHALENE	3.119	14.276	0.518	83.7%	18	Y	25
PHENANTHRENE	14.318	75.378	0.787	152.6%	10	N	25

Samples: 25 Blanks: 2 Duplicates: 1

Table 8d: Polynuclear Aromatic Hydrocarbon Results, 1994 Summary (ng/m³)

Parameter Name	Average	Maximum	Minimum	% RSD	Detect	In Blank?	Reported
BENZO (A)PYRENE	0.017	0.018	0.017	4.6%	0	N	3
CHRYSENE	1.233	2.436	0.030	97.5%	1	N	3
FLUORANTHENE	3.901	4.731	3.070	21.3%	0	N	3
NAPHTHALENE	2.956	5.730	0.182	93.8%	2	Y	3
PHENANTHRENE	35.502	51.322	19.681	44.6%	2	N	3

Samples: 3 Blanks: 1 Duplicates: 0

Table 8e: Polynuclear Aromatic Hydrocarbon Results, 1995 Summary (ng/m³)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE	0.012	0.016	0.008	33.6%	0	N	3
BENZO (A) PYRENE	0.110	0.671	0.008	156.6%	8	Y	18

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
CHRYSENE	0.220	0.736	0.016	92.8%	6	N	18
FLUORANTHENE	3.020	12.889	0.463	93.4%	15	N	18
NAPHTHALENE	2.483	13.848	0.253	133.2%	15	Y	18
PHENANTHRENE	11.833	30.915	1.786	65.7%	17	Y	18

Total Number of Samples: 18 Number of Blanks: 2 Number of Duplicates: 2

In addition to the yearly comparison, enough data is present for a seasonal evaluation of both ambient concentrations and detection rates. This data is presented in the tables below. The data in tables 9a - 9d is presented graphically in Figures 5 and 6 on page 18.

Table 9a: Polynuclear Aromatic Hydrocarbon Results By Season Winter (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE	0.012	0.016	0.008	33.6%	0	N	3
BENZO (A) PYRENE	0.212	3.093	0.008	340.6%	6	N	20
CHRYSENE	12.666	196.941	0.027	364.0%	6	N	20
FLUORANTHENE	4.462	33.620	0.130	170.3%	14	Y	20
NAPHTHALENE	3.392	14.276	0.282	126.4%	16	Y	20
PHENANTHRENE	7.585	19.681	0.787	80.7%	13	N	20
PYRENE	1.645				1	N/A	1

Samples: 20 Blanks: 3 Duplicates: 1

Table 9b: Polynuclear Aromatic Hydrocarbon Results By Season Spring (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE	1.793	4.006	0.371	88.4%	0	N/A	3
BENZO (A) PYRENE	0.100	0.671	0.009	165.5%	12	Y	20
CHRYSENE	0.497	1.681	0.101	70.4%	4	N	20
CORONENE	0.277	0.458	0.143	48.1%	0	N/A	3
FLUORANTHENE	2.048	7.762	0.134	99.5%	12	N	18
NAPHTHALENE	2.231	4.292	0.253	53.5%	14	Y	20
PHENANTHRENE	12.304	106.562	0.805	194.4%	12	Y	20

Samples: 20 Blanks: 2 Duplicates: 1

Table 9c: Polynuclear Aromatic Hydrocarbon Results By Season Summer (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZ (A) ANTHRACENE		1.002			0	N/A	1
BENZO (A) PYRENE	0.044	0.418	0.003	189.9%	15	N	24
CHRYSENE	0.673	4.373	0.016	121.0%	2	N	24
CORONENE		0.206			0	N/A	1
FLUORANTHENE	5.355	22.458	0.147	110.3%	20	N	24
NAPHTHALENE	3.021	22.453	0.180	144.9%	21	Y	24
PHENANTHRENE	17.056	75.378	0.600	125.3%	16	N	24

Samples: 24 Blanks: 1 Duplicates: 3

Table 9d: Polynuclear Aromatic Hydrocarbon Results By Season Autumn (ng/m^3)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
BENZO (A) PYRENE	0.070	0.180	0.008	84.3%	6	N/A	9
CHRYSENE	1.457	5.349	0.030	126.5%	2	N/A	9
FLUORANTHENE	2.730	9.723	0.133	109.0%	5	N/A	9
NAPHTHALENE	2.653	8.336	0.182	99.8%	7	N/A	9
PHENANTHRENE	9.032	51.322	0.800	169.7%	6	N/A	9
PYRENE		2.039			1	N/A	1

Samples: 9 Blanks: 0 Duplicates: 0

Polynuclear Aromatic Hydrocarbons, Quality Assurance Parameters

Results of duplicate and blank samples are documented below. It should be noted that not a single duplicate passes QC criteria of $^+$/.25% for all parameters. For the purposes of this data, a bad pair indicates that one sample was a detect, while the other was not for a particular parameter. A total of 3 bad data pairs were obtained out of 25 total data pairs, indicating that 88.0% of the data pairs were acceptable on this level. Average percent differences for the good pairs are $^+$/- 10.9% for Benzo (a) Pyrene, $^+$/- 25.0% for Chrysene, $^+$/- 58.0% for Fluoranthene, $^+$/- 75.8% for Naphthalene and $^+$/- 26.5% for Phenanthrene.

This situation is being addressed by investigating the use of a combination PUF plug/XAD resin sampling matrix. Studies have shown that some of the PAHs are collected more efficiently on one or the other matrix. The combination matrix is currently being recommended for TO-13 determinations. The addition of XAD resin to the sampling matrix should increase the efficiency of collection.

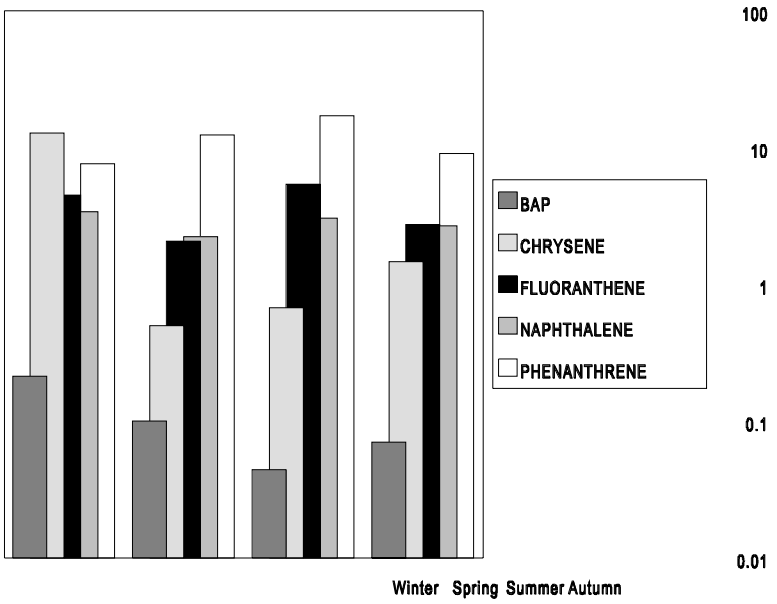
Table 10a: Polynuclear Aromatic Hydrocarbon Duplicate Sample Analysis (ng/m^3)

Parameter Name	Date	Primary	Duplicate	Average %	Difference	Detects?
BENZO (A) PYRENE	06/07/92	0.030	0.044	0.037	37.1%	Y/Y
BENZO (A) PYRENE	09/19/92	0.012	0.012	0.012	1.5%	Y/Y
BENZO (A) PYRENE	01/14/93	0.008	0.008	0.008	1.3%	N/N
BENZO (A) PYRENE	03/04/95	0.047	0.046	0.047	3.8%	N/N
BENZO (A) PYRENE	06/08/95	0.039	0.010	0.024	120.1%	Y/N
CHRYSENE	06/07/92	0.601	4.373	2.487	151.7%	Y/N
CHRYSENE	09/19/92	0.607	0.616	0.611	1.5%	N/N
CHRYSENE	01/14/93	0.531	0.524	0.528	1.3%	N/N
CHRYSENE	03/04/95	0.101	0.291	0.196	97.1%	N/N
CHRYSENE	06/08/95	0.016	0.016	0.016	0.2%	N/N
FLUORANTHENE	06/07/92	0.782	0.344	0.563	77.8%	Y/Y
FLUORANTHENE	09/19/92	0.910	2.957	1.933	105.9%	N/Y
FLUORANTHENE	01/14/93	3.209	1.416	2.312	77.5%	Y/Y
FLUORANTHENE	03/04/95	1.583	3.196	2.389	67.5%	Y/Y
FLUORANTHENE	06/08/95	2.100	2.300	2.200	9.1%	Y/Y
NAPHTHALENE	06/07/92	0.180	1.250	0.715	149.5%	Y/Y
NAPHTHALENE	09/19/92	0.607	0.616	0.611	1.5%	N/N
NAPHTHALENE	01/14/93	4.463	2.779	3.621	46.5%	Y/Y
NAPHTHALENE	03/04/95	1.770	3.937	2.854	76.0%	Y/Y
NAPHTHALENE	06/08/95	1.458	0.453	0.956	105.2%	Y/Y
PHENANTHRENE	06/07/92	4.509	4.217	4.363	6.7%	Y/Y
PHENANTHRENE	09/19/92	0.910	0.924	0.917	1.5%	N/N
PHENANTHRENE	01/14/93	0.797	0.787	0.792	1.3%	N/N
PHENANTHRENE	03/04/95	8.122	20.515	14.318	86.6%	Y/Y
PHENANTHRENE	06/08/95	4.569	6.598	5.584	36.3%	Y/Y

Occasional blanks have shown traces of different parameters. These detects have been evaluated at the average sampling volume (346.8 cubic meters) to determine the level of potential interference. These blanks all exceed the QC limits of 10 ng per PUF. Note that these represent 4 different blanks, out of a total of six submitted.

Table 10b: Polynuclear Aromatic Hydrocarbons in Blank Samples

Parameter Name	Date	uG/PUF	ng/m^3
BENZO ALPHA PYRENE (BAP)	04/04/93	0.013	0.037
BENZO ALPHA PYRENE (BAP)	04/09/95	0.017	0.049
FLUORANTHENE	01/20/93	0.345	0.995
NAPHTHALENE	01/20/93	0.24	0.692
NAPHTHALENE	12/10/94	0.519	1.497
NAPHTHALENE	04/09/95	0.285	0.822
PHENANTHRENE	04/09/95	0.067	0.193


Urban Air Toxics
PAH Seasonal Trends
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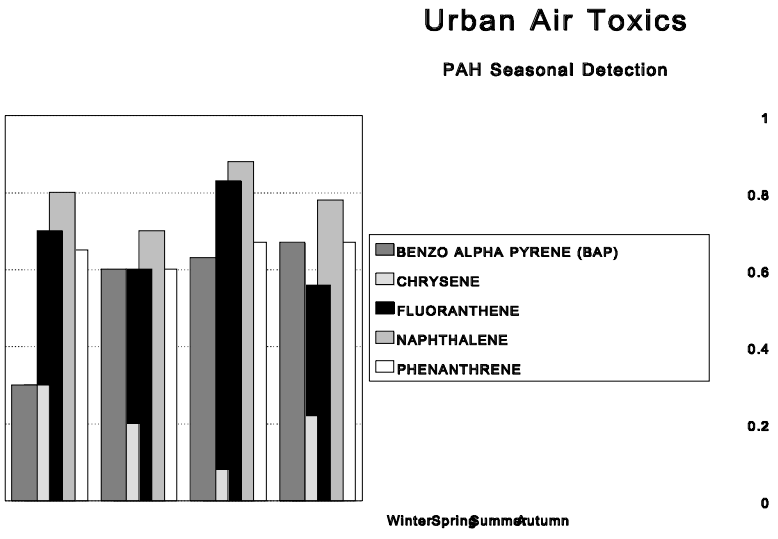
10
1
0.1
0.01
BAP
CHRYSENE
FLUORANTHENE
NAPHTHALENE
PHENANTHRENE
Winter Spring Summer Autumn


Urban Air Toxics
PAH Seasonal Detection
1
0.8
0.6
0.4
0.2
0
BENZO ALPHA PYRENE (BAP)
CHRYSENE
FLUORANTHENE
NAPHTHALENE
PHENANTHRENE
WinterSpringSummerAutumn

Polynuclear Aromatic Hydrocarbons, Data Comparisons

PAHs as a compound class are among the most studied of the air toxics. As such, results from around the world are available for comparison. However, comparison of the data can be complicated by the fact that there are literally hundreds of PAHs, and the various studies may or may not be quantifying the same parameters as the Green Bay study. In addition, there are a variety of sampling methods applicable to these compounds which may result in different profiles of compounds. For these reasons, comparison of "total PAHs" must be carefully performed, and an individual parameter comparison is much more useful.

A representative study performed in the same region is represented through the Lake Michigan Urban Air Toxics Study (LMUATS), conducted in the summer of 1991 in several locations throughout the southern Lake Michigan Region, including downtown Chicago at the Illinois Institute of Technology, at the Kankakee airport upwind of IIT and at South Haven Michigan, along the eastern side of Lake Michigan. Additionally, a research vessel, the RV Laurentian, was used to obtain samples off shore from Chicago.

A comparison between the reported averages of this study and the Green Bay site is shown in the table below. It is important to note that sampling differences may account for greater concentrations of the more volatile PAHs, especially naphthalene, observed in the LMUATS. Results are in ng/m^3.

Table 11: Comparison of WUATM and LMUATS PAH Results (ng/m^3)

Parameter Name	GB AVG	IIT	Kankakee	South Haven	Laurentian
BENZO ALPHA PYRENE (BAP)	0.105	3	0.26	0.13	0.25
CHRYSENE	3.774	5.2	0.33	0.28	0.62
FLUORANTHENE	3.944	47	2.1	1.5	3.2
NAPHTHALENE	2.483	530	330	64	120
PHENANTHRENE	12.299	170	8	4.6	11
PYRENE	1.842	24	1.1	0.75	1.6

Polynuclear aromatic hydrocarbons are derived from a number of sources, both natural and anthropogenic. In general, the anthropogenic sources involve incomplete combustion of organic material. Much work has been done characterizing sources by their PAH composition in an attempt to define "fingerprints" whereby ratios of different compounds present in the air can be used to determine whether the compounds originated from wood smoke, vehicle exhaust or burning coal. This type of characterization requires analyzing for a greater number of parameters than the Green Bay study has to date.

Polychlorinated Biphenyls and Pesticides, Data Completeness

Records for collection of PCB samples begin in September 1991. Samples were not collected between October 10, 1993 and October 11, 1994, in part because of a lack of PUF plug availability.

Project completeness with reference to is documented in the following tables. Table 12 relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. It should be noted that the period of non-sampling noted above is not subtracted out of the sampling days. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days. Figure 7 on page 25 presents the data in table 12 graphically.

Table 12: PCB and Pesticide Sampling Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Sampling Days
Overall	60.4%	76	67	6	3	111
1991	100.0%	10	8	2	0	8
1992	92.9%	27	26	1	0	28
1993	53.3%	17	16	1	0	30
1994	6.7%	2	2	0	0	30
1995	100.0%	20	15	2	3	15

Table 13 documents analytical completeness in terms of results obtained for samples submitted. Reasons for analytical incompleteness may include loss of samples in the laboratory through poor recovery early in the program, and samples misplaced by the sample operator or in the mail system. Completeness in this table is the ratio of Samples to Samples Submitted.

Table 13: PCB and Pesticide Analytical Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Submitted
Overall	97.4%	74	66	5	3	76
1991	90.0%	9	7	2	0	10
1992	103.7%	28	27	1	0	27
1993	100.0%	17	16	1	0	17
1994	0.0%	0	0	0	0	2
1995	100.0%	20	15	2	3	20

Polychlorinated Biphenyls and Pesticides, Analytical Results

Results of all samples were evaluated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. Some 74 sets of results were reported by the laboratory out of a total of 76 samples collected. The table below summarizes results for all reported PCB analytical parameters.

It should be noted that all detects for these parameters occurred after October 1993, when sampling and analytical conditions were altered to improve detection limits. These alterations include improvement of the analytical procedures allowing for lower instrument detections limits (from 1.0 ug/sample to 0.30 ug/sample for total PCBs), and increasing sampling time from 24 to 72 hours. Values are reported in ng/m^3, and represent maximum possible values with non-detects evaluated at the detection limit.

Table 14: PCB/Pesticide Results, Summary of all samples (ng/m^3)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Reported	% Detect
ATRAZINE	0.736	1.152	0.136	50.0%	5	73	6.8%
CHLORDANE	1.070	1.728	0.204	54.4%	0	73	0.0%
DDT	0.337	0.576	0.034	64.5%	0	73	0.0%
DIELDRIN	0.193	1.080	0.034	75.8%	1	72	1.5%
HCB	0.090	0.144	0.008	51.3%	2	73	2.7%
LINDANE	0.174	0.288	0.020	58.7%	9	72	12.5%
TOTAL PCBS	1.746	2.880	0.204	99.9%	15	73	20.5%

Samples: 73 Blanks: 6 Duplicates: 1 Co-located Lab Checks: 1

Figure 8 on page 25 displays the detection information presented in table 14 above. Tables 15a and 15b below document results obtained under the different sampling regimes. Please note that the detects reported under the 24 hour sampling conditions occurred after the analytical detection limits were improved, but before the sampling protocol changed.

Table 15a: PCB Results By Sampling Conditions 24 Hour Samples (ng/m^3) 9/27/91 - 8/17/93

Parameter	Average	Maximum	Minimum	% RSD	Detects	Reported	% Detect
ATRAZINE	0.965	1.152	0.537	15.1%	0	45	0.0%
CHLORDANE	1.448	1.728	0.805	15.1%	0	45	0.0%

Parameter	Average	Maximum	Minimum	% RSD	Detects	Reported	% Detect
DDT	0.474	0.576	0.134	21.4%	0	45	0.0%
DIELDRIN	0.241	0.288	0.134	15.1%	0	45	0.0%
HCB	0.122	0.144	0.080	12.9%	0	45	0.0%
LINDANE	0.238	0.288	0.080	20.1%	2	45	4.4%
TOTAL PCBS	2.409	2.880	0.805	16.6%	2	45	4.4%

Table 15b: PCB Results By Sampling Conditions 72 Hour Samples (ng/m^3) 8/29/93 - present

Parameter	Average	Maximum	Minimum	% RSD	Detects	Reported	% Detect
ATRAZINE	0.243	0.616	0.136	62.2%	5	21	23.8%
CHLORDANE	0.261	0.299	0.204	10.5%	0	21	0.0%
DDT	0.043	0.050	0.034	10.5%	0	21	0.0%
DIELDRIN	0.093	1.080	0.034	238.6%	1	21	4.8%
HCB	0.028	0.045	0.008	24.7%	2	22	9.1%
LINDANE	0.040	0.137	0.020	68.7%	7	21	33.3%
TOTAL PCBS	0.426	1.110	0.204	53.7%	12	22	54.5%

Each detected parameter was also evaluated on the basis of detects only, to provide a clearer picture of what ambient PCB and pesticide concentrations are in this area. It should be noted that the maximum PCB concentration was observed under 24 hour sampling conditions, and thus does not appear elsewhere in these tables. The values tabulated in Table 16 below are presented graphically in Figure 9 on page 25.

Table 16: PCB/Pesticide Results, Summary of all detects (ng/m^3)

Parameter Name	Average	Maximum	Minimum	RSD (%)
ATRAZINE	0.475	0.616	0.231	32.6%
DIELDRIN	1.080			
HEXACHLOROBENZENE	0.023	0.039	0.008	67.5%

Parameter Name	Average	Maximum	Minimum	RSD (%)
LINDANE	0.072	0.137	0.039	19.8%
TOTAL PCBS	0.718	1.998	0.282	58.6%

Insufficient data is available at this time for the determination of yearly and seasonal trends in PCB and pesticide concentrations in Green Bay. Most of the current detects occur in warmer seasons. Changes to the sampling protocol are being evaluated currently in an attempt to obtain positive year round results.

Polychlorinated Biphenyls and Pesticides, Quality Assurance Parameters

Duplicate precision was evaluated for samples wherein detects were noted. Samples without detects were not evaluated, as these comparisons would simply illustrate the precision of our sampling volumes, rather than any more useful information. Note that all samples which meet these criteria show a difference of less than 6%.

Table 17: PCB and Pesticide Results, Duplicate Precision (ng/m^3)

Parameter Name	Primary	Duplicate	Average	% Diff	Detects
ATRAZINE	0.616	0.578	0.597	3.2%	Y/Y
LINDANE	0.078	0.070	0.074	5.7%	Y/Y
TOTAL PCBS (Aroclor)	0.606	0.538	0.572	5.9%	Y/Y
TOTAL PCBS (Aroclor)	0.559	0.557	0.558	0.2%	Y/Y

A single blank PUF cartridge showed traces of PCB. This result is somewhat questionable, however, as the analyst reported at the time that the sample did not appear to be a blank. No clear determination of whether these results represent a true blank can be made at this time. The ng/m^3 value reported is based on an average 72 hour sampling volume of 1160 m^3.

Table 18: PCBs in Blank Samples

Parameter Name	Date	ug/PUF	ng/m^3
Total PCBs	03/22/95	0.39	0.336

Several samples in early 1995 were submitted for GC/MS confirmation of different peaks. One of these showed the apparent presence of hexachlorobenzene (HCB). The GC/MS scan was not able to confirm the presence of HCB, instead indicating an interference by 1,2,3,3A,4,5,6,10B-Octahydrofluoranthene or 6,11-Dihydrodibenz [B,E] Oxepin-11-one. A total of 4 samples may fall into this category, including one which was reported and treated as a positive detect, and three which were reported as interferences and treated as non-detects.

Another sample which was submitted for GC/MS confirmation was the sample from Table 18. GC/MS results were unable to confirm the presence of PCBs at the level in the sample, instead listing a large number of substituted polynuclear aromatic hydrocarbons as tentative identifications. Results were reported out as PCBs based on the GC/ECD chromatograms which clearly show an Arochlor pattern in the analysts opinion.

A final quality control measure exercised for the PCB analysis involved a inter-laboratory comparison between SLOH and the Illinois State Water Survey (ISWS). ISWS performs their PCB analysis on a congener basis, while SLOH provides results as Total PCBs as Arochlor. As such, we requested that SLOH perform both the regular analysis and congener analysis.

Results of this comparison are reported in table 17 above (the lower PCB duplicate). The primary sample was submitted to SLOH, and the results are based upon the Total PCBs as Arochlor, rather than the summation of the congeners. The duplicate sample represents the total of individual congeners as determined by ISWS.

A number of the congeners reported by ISWS were not identified by SLOH, leading to a relatively large discrepancy between the two laboratories. Although this difference (18.7%) is within the $^{+}$/- 25% accuracy determinations, a relative retention time comparison was made between the two sets of chromatograms in an effort to tentatively identify and quantify unlabeled potential PCB congeners in the SLOH data. The table below compares the congener analysis between the two laboratories. In this table, the "Number" column represents the number of peaks identified as congeners or congener pairs.

Table 19: Interlaboratory Congener Analysis Comparison

Congener Analysis	Number	ISWS	SLOH	Difference
Identified by Both	78	556.4	461.3	18.7%
Total	104	567.6	524.8	7.8%

Polychlorinated Biphenyls and Pesticides, Data Comparisons

A significant body of material is available concerning concentrations of various semi-volatile chlorinated organic compounds in ambient air. Among the most revealing studies are those concerning concentrations of various pesticides. In a study conducted by the EPA between 1970 and 1972, dieldrin was found in more than 85% of the air samples tested, with the mean levels ranging from 1 to 2.8 ng/m^3. During the course of the Green Bay study, there has been only a single dieldrin detect (at 1.080 ng/m^3), with a minimum detectable limit of 0.034 ng/m^3.

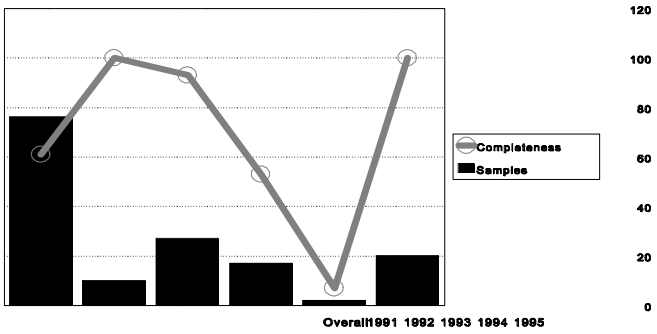
DDT levels in air were determined in 1971 to range from 1 - 2,520 ng/m^3, with the higher values generally coming from southern agricultural areas. This compound has not been detected in Green Bay's air, with detectable quantities ranging from 0.034 - 0.043 ng/m^3 under the 72 hour sampling regime.

PCB studies geographically comparable to the current are somewhat variable. The GLNPO pilot monitoring in Green Bay during the summer of 1989 yielded results which ranged from 3 to 6.5 ng/m^3, with a 77.5% detection rate. Meanwhile, a range 0.6 to 1.8 ng/m^3 was obtained from a study conducted along the shore of Lake Superior in northern Wisconsin and Upper Michigan in 1984. A set of 1983 data from an island in Lake Superior has a range of 1.5 to 5.2 ng/m^3 with an average of 3.2 ng/m^3.

The PCB concentrations determined by this sampling program is in general lower than those above, ranging from 0.282 to 1.998 ng/m^3, with an average of 0.718 ng/m^3. Whether this is an indication that ambient loads of PCBs are diminishing in the Green Bay area can not be determined at this time, as we have an insufficient record of actual detects to track current trends. It should be noted that the rate of detection has increased substantially since the method protocol was changed from a 24 hour to a 72 hour sampling period.

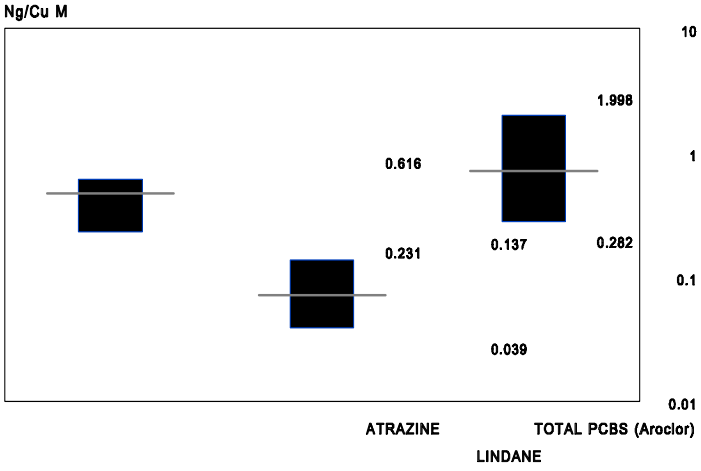
URBAN AIR TOXICS

PCB Completeness



URBAN AIR TOXICS

PCB Parameter Values



Dioxins and Furans, Data Completeness

A total of 12 monthly dioxin samples were collected between 12/91 and 11/92 at the Bay Beach site in Green Bay. Three monthly samples were saved and composited to form each of 4 quarterly composite samples. Sampling at that time was discontinued. Completeness for this parameter is 100%, both in sampling and analysis.

Analytical parameters include total tetra- through octa- chloro dibenzo- dioxins and furans, along with a number of specific isomers. At least some parameters were detected in each sample.

Dioxins and Furans, Analytical Results

Results of the composite samples are presented in the following tables. The first table presents the actual results in pg/m^3. Note that non-detects are evaluated as zero in this table. As such, the reported values represent actual concentrations obtained during the sampling. The results presented in the following table are blank corrected.

Table 20: Dioxin and Furan Results (pg/m^3)

Parameter	mean	max.	min.	RSD	Detects	In Blank?
TCDFs (total)	0.1096	0.2067	0.0560	52.7%	4	Y
2,3,7,8-TCDF	0.0053	0.0081	0.0024	40.3%	4	N
PeCDFs (total)	0.0626	0.1616	0.0000	100.9%	3	N
1,2,3,7,8-PeCDF	0.0000	0.0000	0.0000		0	N
2,3,4,7,8-PeCDF	0.0032	0.0106	0.0000	136.7%	2	N
HxCDFs (total)	0.0451	0.1119	0.0000	95.1%	3	N
1,2,3,4,7,8-HxCDF	0.0027	0.0087	0.0000	133.7%	2	N
1,2,3,6,7,8-HxCDF	0.0003	0.0012	0.0000	173.2%	1	N
2,3,4,6,7,8-HxCDF	0.0033	0.0099	0.0000	122.0%	2	N
1,2,3,7,8,9-HxCDF	0.0000	0.0000	0.0000		0	N
HpCDFs (total)	0.0295	0.0560	0.0000	70.8%	3	N
1,2,3,4,6,7,8-HpCDF	0.0260	0.0528	0.0000	72.6%	3	N
1,2,3,4,7,8,9-HpCDF	0.0000	0.0000	0.0000		0	N
OCDF	0.0291	0.0653	0.0000	80.7%	3	N
TCDDs (total)	0.0017	0.0211	-0.0125	703.9%	4	Y
2,3,7,8-TCDD	0.0000	0.0000	0.0000		0	Y
PeCDDs (total)	0.0174	0.0528	0.0000	123.9%	2	N
1,2,3,7,8-PeCDD	0.0000	0.0000	0.0000		0	N
HxCDDs (total)	0.0520	0.1274	0.0000	97.5%	3	N
1,2,3,4,7,8-HxCDD	0.0000	0.0000	0.0000		0	N
1,2,3,6,7,8-HxCDD	0.0030	0.0118	0.0000	173.2%	1	N
1,2,3,7,8,9-HxCDD	0.0022	0.0087	0.0000	173.2%	1	N
HpCDDs (total)	0.1289	0.2509	0.0117	69.8%	4	Y
1,2,3,4,6,7,8-HpCDD	0.0609	0.1138	0.0070	65.8%	4	Y
OCDD	0.3201	0.5533	0.1623	51.3%	4	Y

Estimations of the toxic potency of complex mixtures of dioxins have been the subject of much research. A variety of Toxicity Equivalence Factors (TEFs) have been generated by different groups. The purpose of the TEFs is to relate the complex mixture to the 2,3,7,8- TCDD. The second table presents a summation of two different calculations of the 2,3,7,8 TCDD toxic equivalents for each sample. The first set of TEFs was developed through international accord in 1989, while the second represents values used by the US EPA beginning in 1987. The basic unit for the TEFs is pg-2,3,7,8-TCDD Equivalent / pg, so that the resulting values are pg-2,3,7,8-TCDD Equivalent.

Table 21: 2,3,7,8-TCDD Toxic Equivalents for Green Bay Samples

Parameter Name	I-TEF	mean TE	TEF (EPA)	mean TE
TCDFs (total)	0	0	0.001	0.0001
2,3,7,8-TCDF	0.1	0.0005	0.1	0.0005
PeCDFs (total)	0	0	0.001	0.00006
1,2,3,7,8-PeCDF	0.5	0	0.1	0
2,3,4,7,8-PeCDF	0.05	0.0002	0.1	0.0003
HxCDFs (total)	0	0	0.0001	0.000004
1,2,3,4,7,8-HxCDF	0.1	0.0003	0.01	0.00003
1,2,3,6,7,8-HxCDF	0.1	0	0.01	0.000003
2,3,4,6,7,8-HxCDF	0.1	0.0003	0.01	0.00003
1,2,3,7,8,9-HxCDF	0.1	0	0.01	0
HpCDFs (total)	0	0	0.00001	0.0000003
1,2,3,4,6,7,8-HpCDF	0.01	0.0003	0.001	0.00003
1,2,3,4,7,8,9-HpCDF	0.01	0	0.001	0
OCDF	0.001	0	0	0
TCDDs (total)	0	0	0.01	0.00002
2,3,7,8-TCDD	1	0	1	0
PeCDDs (total)	0	0	0.005	0.00009
1,2,3,7,8-PeCDD	0.5	0	0.5	0
HxCDDs (total)	0	0	0.0004	0.000008
1,2,3,4,7,8-HxCDD	0.1	0	0.04	0
1,2,3,6,7,8-HxCDD	0.1	0.0003	0.04	0.0001
1,2,3,7,8,9-HxCDD	0.1	0.0002	0.04	0.00009
HpCDDs (total)	0	0	0.00001	0.000001
1,2,3,4,6,7,8-HpCDD	0.01	0.0006	0.001	0.00006
OCDD	0.001	0.0003	0	0
2,3,7,8 TCDD Toxic Equivalents		**0.0031**		**0.0015**

Dioxins and Furans, Quality Assurance Parameters

There were no duplicate samples obtained for these parameters. A single field blank was submitted. Several parameters were detected in this sample, as reported in the following table.

In addition, each sample was run with a method blank composed of a clean PUF plug and filter which had not left the lab. It should be noted that the results reported in table 20 above are blank corrected. The pg/m3 values are based on an average sampling volume of 3500 m^3, and represent the minimum ambient level which was distinguishable from the blank. Each sample consists of three PUF plugs, so that the blank level is multiplied by three in both table 20 and table 22. The method blanks performed at the laboratory had no detectable parameters.

Table 22: Dioxins and Furans in Blank Samples

Parameter Name	pg/sample	pg/m^3
TCDFs (total)	15	0.013
TCDDs (total)	24	0.021
2,3,7,8-TCDD	24	0.021
HpCDDs (total)	31	0.027
1,2,3,4,6,7,8-HpCDD	18	0.015
OCDD	140	0.120

Polar Organic Compounds, Carbonyl Data Completeness

Records for collection of formaldehyde samples begin in July 1991 and continue through the present. Project completeness with reference to formaldehyde is documented in the following tables. The first table relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days. A completeness greater than 100% indicates that extra samples were obtained during that time period.

Table 23: Carbonyl Sampling Completeness

	Completeness	Samples	Ambient	Blanks	Duplicates	Sampling Days
Overall	81.6%	107	93	7	7	114
1991	100.0%	14	12	1	1	12
1992	100.0%	32	28	2	2	28
1993	106.9%	35	31	2	2	29
1994	23.3%	7	7	0	0	30
1995	100.0%	19	15	2	2	15

The following table documents analytical completeness in terms of results obtained for samples submitted. Reasons for analytical incompleteness may include loss of samples in the laboratory through poor recovery early in the program, and samples misplaced by the sample operator or in the mail system.

Table 24: Carbonyl Analytical Completeness

	Completeness	Samples	Ambient	Blanks	Duplicates	Samples Submitted
Overall	94.4%	101	90	5	6	107
1991	100.0%	14	12	1	1	14
1992	96.9%	31	29	1	1	32
1993	97.1%	34	31	1	2	35
1994	57.1%	4	4	0	0	7
1995	94.7%	18	14	2	2	19

Polar Organic Compounds, Carbonyl Analytical Results

Results for aldehyde analysis of all samples are presented in the following table. It should be noted that Acetaldehyde, Acetone and Acrolein have only been reported as values in 1995 analyses, although they have often been cited as present in the samples. As such, only formaldehyde is considered in the site specific, yearly and seasonal data presentation. Please note that all values are in ug/m^3. Data presented in this table is shown graphically in Figure 12 on page 31.

Table 25: Carbonyl Results (ug/m^3)

Parameter	Average	Maximum	Minimum	% RSD	Detects	Reported
ACETALDEHYDE	1.884	5.706	0.362	76.9%	19	19
ACETONE	2.423	7.609	0.148	70.2%	17	19
ACROLEIN	0.145	0.209	0.114	26.8%	0	4
FORMALDEHYDE	2.622	57.064	0.067	340.9%	91	95

Number of Samples 95 Number of Blanks 4 Number of Duplicates 6

Formaldehyde results by site are presented in the table below. It appears that the Fox River site has a higher average level of formaldehyde than the Bay Beach site. This could be related to the fact that the Fox River site is located in a parking lot near traffic centers, while the Bay Beach site was more isolated in this respect.

Table 26: Formaldehyde by Site (ug/m^3)

Site	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported

Site	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
Bay Beach	0.845	7.972	0.067	144.9%	44	N	48
Fox River	4.520	57.064	0.135	276.9%	44	Y	47

Formaldehyde results by year are shown in the table below. Results from 1994 appear to be skewed by the presence of very few samples, and the highest single value. Disregarding 1994 as a year with too few samples to make a clear statement, it appears that the 1993 average is significantly higher than those of 1991 and 1992. It was in 1993 that the site moved from Bay Beach to the Fox River site. Note also the increase of the minima of 1993, 1994 and 1995 over the levels of 1991 and 1992.

Table 27: Formaldehyde by Year (ug/m^3)

Year	Average	Maximum	Minimum	% RSD	Detects	in Blank?	Reported
1991	0.584	2.090	0.067	96.7%	13	N	14
1992	0.909	7.972	0.095	161.4%	25	N	28
1993	3.588	55.671	0.135	311.2%	31	Y	32
1994	19.160	57.064	0.236	117.9%	4	N/A	4
1995	1.159	3.262	0.445	67.0%	15	N	18

Seasonal variations of formaldehyde are displayed in the following table. Summer values are significantly lower than those of the other seasons, while the rest of the seasons can't be distinguished from each other on the basis of the available data.

Table 28: Formaldehyde by Season (ug/m^3)

Season	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
Winter	2.845	33.747	0.118	240.3%	24	N	28
Spring	3.583	55.671	0.135	320.3%	21	N	23
Summer	0.712	2.090	0.135	66.0%	28	Y	28
Autumn	4.159	57.064	0.067	328.7%	15	N/A	16

Polar Organic Compounds, Carbonyl Quality Assurance Parameters

Quality control data generated in the course of aldehyde sampling is documented in the following tables. The first table shows the results of all duplicate sample pairs, along with their averages and each set's percent difference from the average. With one exception, all duplicates are within $^{+}/_{-}$15%.

Table 29: Carbonyl Duplicates (ug/m³)

Duplicate Precision	Primary	Duplicate	Average	% Diff	Detects
ACETALDEHYDE	0.750	0.972	0.861	12.9%	Y/Y
ACETALDEHYDE	2.274	2.455	2.365	3.8%	Y/Y
ACETONE	2.307	2.357	2.332	2.1%	Y/Y
ACETONE	2.175	2.062	2.119	5.3%	Y/Y
FORMALDEHYDE	0.200	0.148	0.174	14.9%	Y/Y
FORMALDEHYDE	0.478	0.507	0.493	3.0%	Y/Y
FORMALDEHYDE	0.859	0.999	0.929	7.5%	Y/Y
FORMALDEHYDE	33.747	1.382	17.564	92.1%	Y/Y
FORMALDEHYDE	0.558	0.599	0.578	3.6%	Y/Y
FORMALDEHYDE	0.643	0.550	0.596	7.8%	Y/Y

The table below presents results from the occasional blanks which have shown traces of different parameters. These detects have been evaluated at the average sampling volume (1.053 m³) to determine the level of potential interference. It should be noted that none of these blanks exceed the generally accepted QC limits of 1 ug/cartridge, and that the last two formaldehyde values (01/03 and 04/09/95) were reported as less than or equal to values, implying the presence of interferences that may not represent true formaldehyde levels.

Table 30: Carbonyls in Blank Samples

PARAMETER NAME	Start Date	ug/sample	(ug/m³)
ACETALDEHYDE	01/03/95	0.1	0.095
ACETALDEHYDE	04/09/95	0.61	0.579
FORMALDEHYDE	07/06/93	0.07	0.066
FORMALDEHYDE	01/03/95	0.1	0.095

FORMALDEHYDE	04/09/95	0.11	0.104

Polar Organic Compounds, Hydrogen Sulfide Data Completeness

Hydrogen sulfide samples were collected between July 1991 and January 1994. Sampling for this parameter was discontinued for lack of positive results. Project completeness with reference to hydrogen sulfide is documented in the following tables. The first table relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days.

URBAN AIR TOXICS

Aldehyde Parameter Values

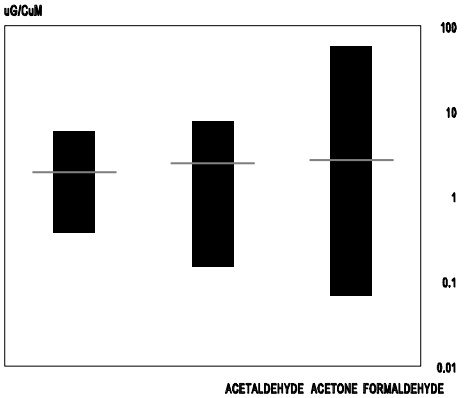


Table 31: Hydrogen Sulfide Completeness

	Completeness	Samples	Ambient	Blanks	Duplicates	Sampling Days
Overall	98.6%	152	72	67	13	73
1991	100.0%	30	12	12	6	12
1992	100.0%	58	29	27	2	29
1993	96.6%	58	28	25	5	29
1994	100.0%	6	3	3	0	3

The following table documents analytical completeness in terms of results obtained for samples submitted. Reasons for analytical incompleteness may include loss of samples in the laboratory through poor recovery early in the program, and samples misplaced by the sample operator or in the mail system.

Table 32: Hydrogen Sulfide Analytical Completeness

	Completeness	Samples	Ambient	Blanks	Duplicates	Samples Submitted
Overall	94.1%	143	65	70	8	152
1991	90.0%	27	12	10	5	30
1992	96.6%	56	28	27	1	58
1993	93.1%	54	22	30	2	58
1994	100.0%	6	3	3	0	6

Polar Organic Compounds, Hydrogen Sulfide Analytical Results

During the entire monitoring period, there was not a single sample which showed a detectable level of hydrogen sulfide. Detection limits were 0.001 ppm. Sampling was discontinued for lack of results.

Polar Organic Compounds, Phenol Data Completeness

Phenol samples were collected between July 1991 and January 1994. Sampling for this parameter was discontinued for lack of positive results. Project completeness with reference to phenol is documented in the following tables. The first table relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days.

Table 33: Phenol Sampling Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Sampling Days
Overall	90.3%	120	65	50	5	72
1991	83.3%	24	10	10	4	12
1992	93.1%	53	27	26	0	29
1993	89.7%	41	26	14	1	29
1994	100.0%	2	2	0	0	2

The following table documents analytical completeness in terms of results obtained for samples submitted. The overall completeness for this parameter is among the best for all of the study program at 96.7%.

Table 34: Phenol Analytical Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Samples Submitted
Overall	96.7%	116	62	48	6	120
1991	108.3%	26	11	10	5	24
1992	84.9%	45	24	21	0	53
1993	104.9%	43	25	17	1	41
1994	100.0%	2	2	0	0	2

Polar Organic Compounds, Phenol Analytical Results

Results for phenol analysis are presented in the following table. This table includes two sections, the first showing results of all samples reported as maximum potential values, and the second showing results of only the detects, thus representing actual values. Results are reported as ug/m^3. It should be noted that raw laboratory results from the impinger analyses are reported on the basis of ug/ml solution, thus requiring the volume of the solution remaining at the time of analysis to calculate the total ug/sample.

Table 35: Phenol Results (ug/m^3)

	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported
PHENOL	0.712	4.565	0.045	94.2%	14	Y	119
detects	0.314	2.333	0.061	214.3%			

	Average	Maximum	Minimum	% RSD	Detects	In Blank?	Reported

Polar Organic Compounds, Phenol Quality Assurance Parameters

There were no incidences of detects involving phenol duplicates, so that there are no results to report. Several of the 14 detects involved blanks, however. These are reported in the table below, with the ug/m^3 calculation based on the average sampling volume of 0.95 m^3.

Table 36: Phenol in Blank Samples

Parameter	Date	ug/sample	ug/Cu M
PHENOL	08/19/91	0.145	0.153
PHENOL	06/13/92	0.4	0.421
PHENOL	07/09/92	0.08	0.084
PHENOL	08/29/93	0.04	0.042

Volatile Organic Compounds, Data Completeness

VOC samples were collected using adsorbent tubes between July 1991 and September 1993, and between July 1994 and the present using passivated stainless steel canisters. No samples were collected between September 1993 and July 1994. Many adsorbent tube samples were lost during the analytical stage from difficulties with the thermal desorption apparatus.

Project completeness with reference to VOCs is documented in the following tables. The first table relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. It should be noted that the period of non-sampling which occurred while the method was being changed is subtracted out of the sampling days. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days.

Table 37: VOC Sampling Completeness

Completeness		Samples	Ambient	Blanks	Duplicates	Sampling Days
Adsorbents	86.7%	258	52	49	157	60
Canisters	70.0%	23	21		2	30

Table 38 documents analytical completeness in terms of results obtained for samples submitted. Reasons for analytical incompleteness may include loss of samples in the laboratory through poor recovery, and samples misplaced by the sample operator or in the mail system. Completeness in

this table is the ratio of Samples to Samples Submitted.

Table 38: VOC Analytical Completeness

Completeness	Samples	Ambient	Blank	Duplicates	Submitted
Adsorbents	52.7%	136	44	41	51	258
Canisters	56.5%	13	13	0	0	23

Table 39 below represents compounds reported during the sampling program. The first column, "Ads Detects", indicates the number of detects observed for a particular parameter during the adsorbent tube sampling phase, followed by the number of samples evaluated for this purpose. The next column, "Can Detects", tallies the detected parameters from the canister portion of the test, along with the number of samples for which the named parameter was included in the database. The final pair of columns indicates the same for PAMS compounds reported from canister samples.

It should be noted that the number of samples indicated in their respective columns do not necessarily represent all times a particular parameter has been reported during this project. Many non-detected parameters have simply been excluded from the database to save space. A listing of all VOC parameters reported at any time is included as Table 40 below.

Table 39: VOC Detection

Parameter	Ads Detects	Samples	Can Detects	Samples	PAMS Detects	Samples
1,1,1-TRICHLOROETHANE	19	38	12	12		
1,1,2,2-TETRACHLOROETHANE			1	7		
1,3 BUTADIENE			0	6	7	7
1,3 BUTADIENE	2	38				
1,4-DICHLOROBENZENE	36	38	0	6		
ACETYLENE			6	6	6	6
ALPHA - PINENE	30	38				
BENZENE	21	38	12	12	7	7
BROMOMETHANE			1	6		
BUTANOL	21	38				
CARBON TETRACHLORIDE			12	12		
CHLOROFORM	31	38	4	8		
CUMENE (I-PROPYLBENZENE)	34	38	1	6	2	3
ETHANOL	24	38				
ETHYLBENZENE			11	11		
ISOPROPANOL	34	38				
LIMONENE	31	38				
METHYLCHLORIDE			4	7		
METHYLENE CHLORIDE	18	38	6	8		
N-HEXANE	22	38			7	7
PROPENE			6	6		
STYRENE	19	38	7	11	5	6
TETRACHLOROETHENE	24	38	5	8		

TOLUENE	25	38	12	12	7	7
TRICHLOROETHENE	13	38	1	6		
XYLENES (m & p)	23	38	12	12	7	7
n-OCTANE			6	6	7	7
o-XYLENE			12	12	7	7

It should also be noted that not all of the VOC parameters reported in this program are considered toxic compounds. A significant amount of PAMS (photochemical assessment monitoring) analysis has been performed on the samples. The parameters which are a part of this monitoring program are not necessarily considered toxic. Results have been reported in this report as they represent data pertaining to the characterization of Green Bay's atmosphere.

Table 40: Reported VOC Parameters

PARAMETER NAME	PARAMETER NAME	PARAMETER NAME
1,1,1-TRICHLOROETHANE	2-METHYLPENTANE	I-BUTENE
1,1,2,2-TETRACHLOROETHANE	3-ETHYLHEXANE	I-PENTANE
1,1,2-TRICHLOROETHANE	3-METHYL-1-BUTENE	ISOPRENE
1,1-DICHLOROETHANE	3-METHYLHEPTANE	ISOPROPANOL
1,2,4-TRIMETHYLBENZENE & sec-BUTYLB	3-METHYLHEXANE	LIMONENE
1,2-DICHLOROBENZENE	3-METHYLPENTANE	m-ETHYLTOLUENE
1,2-DICHLOROETHANE	4-METHYL-1-PENTENE	METHANE
1,2-DICHLOROPROPANE	ACETYLENE	METHYL ETHYL KETONE
1,3 BUTADIENE	ALPHA - PINENE	METHYLCHLORIDE
1,3,5-TRIMETHYLBENZENE	BENZENE	METHYLCYCLOHEXANE
1,3-DICHLOROBENZENE	beta-PINENE	METHYLCYCLOPENTANE
1,4-DICHLOROBENZENE	BROMODICHLOROMETHANE	METHYLENE CHLORIDE
1-BUTENE	BROMOFORM	N-BUTANE
1-HEXENE	BROMOMETHANE	N-DECANE
1-PENTENE	BUTANOL	n-HEPTANE
2,2,4-TRIMETHYLHEXANE	c-1,3-DICHLOROPROPENE	N-HEXANE
2,2,4-TRIMETHYLPENTANE	CARBON TETRACHLORIDE	n-NONANE
2,2-DIMETHYLBUTANE	CHLOROBENZENE	n-OCTANE
2,2-DIMETHYLHEPTANE	CHLOROETHANE	n-PENTANE
2,2-DIMETHYLPROPANE	CHLOROFORM	n-PROPYLBENZENE
2,3,4-TRIMETHYLPENTANE	CHLOROPRENE	o-ETHYLTOLUENE
2,3-DIMETHYLBUTANE	cis-2-BUTENE	o-XYLENE
2,3-DIMETHYLHEXANE	cis-2-HEXENE	p-ETHYLTOLUENE
2,3-DIMETHYLPENTANE	cis-2-PENTENE	PROPANE
2,4,4-TRIMETHYL-1-PENTENE	cis-4-METHYL-2-PENTENE	PROPENE
2,4,4-TRIMETHYL-2-PENTENE	CUMENE (I-PROPYLBENZENE)	STYRENE
2,4-DIMETHYLHEXANE	CYCLOHEXANE	t-1,2-DICHLOROETHENE
2,4-DIMETHYLPENTANE	CYCLOPENTANE	t-1,3-DICHLOROPROPENE
2,5-DIMETHYLHEXANE	CYCLOPENTENE	TETRACHLOROETHENE
2-BUTANOL	DIBROMOCHLOROMETHANE	TOLUENE
2-METHYL-1-BUTENE	ETHANE	trans-2-BUTENE
2-METHYL-1-PENTENE	ETHANOL	trans-2-HEXENE
2-METHYL-2-BUTENE	ETHYLBENZENE	trans-2-PENTENE

2-METHYL-2-PENTENE	ETHYLCYCLOHEXANE	TRICHLOROETHENE
2-METHYLHEPTANE	ETHYLENE	VINYL CHLORIDE
2-METHYLHEXANE	I-BUTANE	XYLENES (m & p)

Volatile Organic Hydrocarbons, Toxics Analytical Results

The tables following represent summation on the basis of method and analysis type (adsorbent tubes, and canisters, both Toxics and PAMS parameters). In addition, comparison tables include a comparison of results from the toxics analysis, and a comparison of PAMS results from the Green Bay site and the three Wisconsin PAMS sites. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. It should be noted that most non-detects are not included in these evaluations, as such results frequently were not incorporated into the database.

Additional reporting criteria include the number of detects, how many samples reported each particular parameter, and, in the case of the adsorbent tubes, how many "bad pairs" were present. Each adsorbent tube sample reported represents the results of two individual tubes collected at the same time. A membership value was determined for each pair of data. The membership value is determined by a one dimensional Gaussian function and evaluated by Fuzzy Set Theory, as recommended by Walling.

Fuzzy Set theory assumes there is a continuous range of values reflecting the certainty in a measurement, rather than discrete values of certainty. Bad pairs of data are those whose membership values fall outside of the acceptable range. In general, a membership of greater than 0.65 is required for the values to be evaluated as valid. (A membership value of 1 implies an uncomplicated sample). Values are reported as ppbv.

Table 41: VOC Analytical Results, Adsorbent Tubes (ppbv)

Parameter, Adsorbent Tubes	Avg	Max	Min	RSD	Detects	Samples	Bad Pairs
ALPHA - PINENE	0.713	8.626	0.000	207.6%	30	38	14
N-HEXANE	0.708	17.284	0.000	404.4%	22	38	9
LIMONENE	0.428	1.829	0.000	103.1%	31	38	14
1,4-DICHLOROBENZENE	0.352	1.736	0.000	110.1%	36	38	13
ISOPROPANOL	0.336	3.570	0.000	175.7%	34	38	9
TOLUENE	0.296	3.007	0.000	201.4%	25	38	7
BENZENE	0.160	1.177	0.000	156.6%	21	38	6
XYLENES (m & p)	0.152	1.229	0.000	200.0%	23	38	9
CHLOROFORM	0.146	0.590	0.000	90.4%	31	38	18
METHYLENE CHLORIDE	0.129	1.414	0.000	220.7%	18	38	3
ETHANOL	0.113	2.000	0.000	316.6%	24	38	7
1,1,1-TRICHLOROETHANE	0.058	0.441	0.000	180.9%	19	38	5
CUMENE (I-PROPYLBENZENE)	0.053	0.199	0.000	115.5%	34	38	11
TETRACHLOROETHENE	0.027	0.127	0.000	126.1%	24	38	2
TRICHLOROETHENE	0.027	0.432	0.000	298.7%	13	38	4
BUTANOL	0.016	0.130	0.000	168.5%	21	38	4
STYRENE	0.016	0.207	0.000	229.8%	19	38	6
1,3 BUTADIENE	0.000	0.000	0.000	0.0%	2	38	0

The table below presents data generated from toxics parameter analysis of canister samples obtained between 7/94 and 6/95. Values are reported as ppbv.

Table 42: VOC Analytical Results, Passivated Stainless Steel Canisters (ppbv)

Parameters, Canisters	Average	Maximum	Minimum	%RSD	Detects	Reported
ACETYLENE	2.47	4.70	0.47	65.4%	6	6
TOLUENE	0.90	2.00	0.20	59.1%	12	12
PROPENE	0.65	1.16	0.17	52.0%	6	6
BENZENE	0.61	1.40	0.30	48.1%	12	12
XYLENES (m & p)	0.43	0.80	0.20	46.5%	12	12
1,1,1-TRICHLOROETHANE	0.36	0.70	0.20	41.8%	12	12
o-XYLENE	0.18	0.30	0.10	43.6%	12	12
ETHYLBENZENE	0.15	0.30	0.10	45.1%	11	11
METHYLENE CHLORIDE	0.11	0.20	0.00	69.4%	6	8
STYRENE	0.11	0.40	0.00	106.7%	7	11
CARBON TETRACHLORIDE	0.10	0.10	0.10	0.0%	12	12
METHYLCHLORIDE	0.10	0.30	0.00	106.9%	4	7
n-OCTANE	0.08	0.09	0.04	22.8%	6	6
TETRACHLOROETHENE	0.08	0.20	0.00	88.2%	5	8
CHLOROFORM	0.05	0.10	0.00	100.0%	4	8
BROMOMETHANE	0.03	0.20	0.00	223.6%	1	6
CUMENE (I-PROPYLBENZENE)	0.03	0.20	0.00	223.6%	1	6
TRICHLOROETHENE	0.03	0.20	0.00	223.6%	1	6
1,1,2,2-TETRACHLOROETHANE	0.01	0.10	0.00	244.9%	1	7

Comparison of the two tables above shows clearly that parameter lists used for these analyses were not identical. The table below compares the adsorbent and canister results for all parameters which were detected in both types of analysis. Values are reported as ppbv.

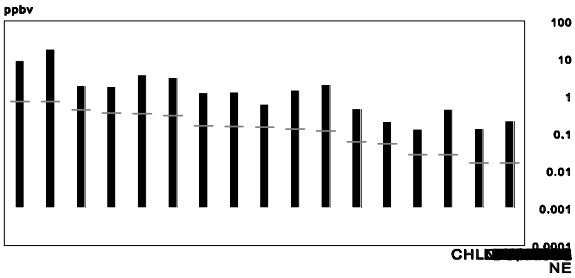
Table 43: VOC Analytical Results Comparison

TOXIC PARAMETERS	Canisters Avg	Adsorbents Avg
1,1,1-TRICHLOROETHANE	0.36	0.058
BENZENE	0.61	0.160
CHLOROFORM	0.05	0.146
CUMENE (I-PROPYLBENZENE)	0.03	0.053
METHYLENE CHLORIDE	0.11	0.129
STYRENE	0.11	0.016
TETRACHLOROETHENE	0.08	0.027
TOLUENE	0.90	0.296
TRICHLOROETHENE	0.03	0.027
XYLENES (m & p)	0.43	0.152

The preceding three tables are illustrated in the figures on the following page.

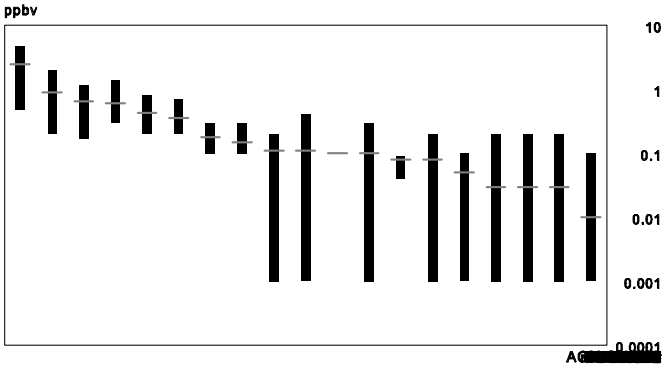
URBAN AIR TOXICS

VOC Parameter Values, Adsorbent Tubes



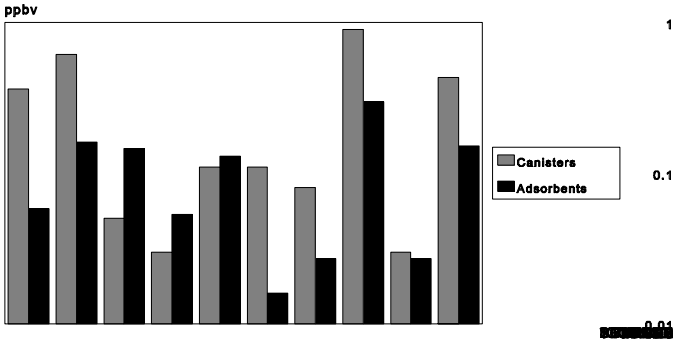
URBAN AIR TOXICS

VOC Parameter Values, Canisters



URBAN AIR TOXICS

VOC Parameter Comparison



Volatile Organic Hydrocarbons, PAMS Analytical Results

In addition to the toxics parameters reported, a number of the canister samples sent to BRC were analyzed for PAMS compounds also. Results from these analysis are reported in the table below. Please note that the units for PAMS analysis is ppbc, as opposed to ppbv.

Table 44: VOC PAMS Analytical Results (ppbc)

Parameter Name	Average	Maximum	Minimum	% RSD	Detects	Reported
TOTAL NMHC	181.4	410.9	96.7	58.2%	6	6
TOTAL UNIDENTIFIED NMHC	49.5	80.7	29.6	32.2%	6	6
N-HEXANE	32.2	104.6	2.1	96.9%	7	7
N-BUTANE	13.0	53.3	2.5	128.5%	7	7
I-PENTANE	8.1	31.0	2.1	116.7%	7	7
ETHANE	6.1	8.1	4.8	17.3%	7	7
TOLUENE	6.0	15.2	2.8	65.3%	7	7
PROPANE	5.7	10.0	2.4	45.9%	7	7
ACETYLENE	4.9	7.2	2.8	31.7%	6	6
ETHYLENE	3.6	6.3	1.6	48.0%	7	7
XYLENES (m & p)	3.1	5.8	0.7	52.0%	7	7
n-PENTANE	2.9	8.6	1.1	82.1%	7	7
BENZENE	2.6	4.5	1.6	41.2%	7	7
METHYLCYCLOPENTANE	2.5	4.2	0.6	46.7%	7	7
3-METHYLPENTANE	2.2	5.2	0.6	62.7%	7	7
2-METHYLPENTANE	2.2	6.0	0.8	77.8%	7	7
1,2,4-TRIMETHYLBENZENE & sec-BUTYLB	2.0	3.9	0.8	48.6%	7	7
I-BUTANE	2.0	6.2	0.6	90.7%	7	7
2,2,4-TRIMETHYLPENTANE	1.9	3.6	1.1	44.2%	7	7
3-METHYLHEXANE	1.8	2.6	0.6	37.5%	7	7
o-XYLENE	1.4	3.0	0.7	53.4%	7	7
PROPENE	1.4	2.5	0.6	47.0%	7	7
STYRENE	1.3	3.5	0.0	81.2%	5	6
p-ETHYLTOLUENE	1.2	2.0	0.7	34.7%	6	6
2,3-DIMETHYLPENTANE	1.1	1.9	0.6	39.9%	7	7
ETHYLBENZENE	1.1	1.9	0.5	40.5%	7	7
2,3,4-TRIMETHYLPENTANE	1.1	3.9	0.3	107.6%	7	7
o-ETHYLTOLUENE	0.8	1.0	0.6	17.0%	3	3
2-METHYLHEXANE	0.8	1.6	0.2	55.0%	7	7
2-METHYL-2-BUTENE	0.8	2.4	0.2	100.3%	6	6
trans-2-PENTENE	0.7	2.3	0.2	108.0%	6	6
2,3-DIMETHYLBUTANE	0.7	1.9	0.3	79.2%	7	7
1,3,5-TRIMETHYLBENZENE	0.7	1.2	0.3	45.1%	6	6
n-HEPTANE	0.6	1.5	0.3	57.5%	7	7
2,4-DIMETHYLPENTANE	0.6	1.1	0.4	40.5%	7	7
I-BUTENE	0.6	1.0	0.4	30.3%	7	7
n-NONANE	0.6	0.8	0.3	31.1%	6	6
METHYLCYCLOHEXANE	0.5	0.9	0.3	47.7%	5	5
m-ETHYLTOLUENE	0.5	0.9	0.3	35.4%	6	6
2-METHYL-1-BUTENE	0.5	1.9	0.2	108.8%	7	7
n-OCTANE	0.5	0.7	0.2	33.8%	7	7
n-PROPYLBENZENE	0.5	0.8	0.2	36.5%	6	6
CYCLOHEXANE	0.4	0.7	0.2	40.8%	6	6
cis-2-PENTENE	0.4	1.0	0.1	77.5%	5	5
2-METHYLHEPTANE	0.4	0.5	0.2	25.8%	5	5
2,4-DIMETHYLHEXANE	0.4	0.7	0.0	67.4%	4	5
2,2-DIMETHYLBUTANE	0.4	0.6	0.1	46.4%	6	6
1-PENTENE	0.4	1.0	0.0	92.9%	5	6
3-ETHYLHEXANE	0.3	0.6	0.0	74.5%	3	4
2,4,4-TRIMETHYL-1-PENTENE	0.3	0.3	0.3	0.00	2	2
1,3 BUTADIENE	0.3	0.6	0.1	51.0%	7	7
CYCLOPENTANE	0.3	0.8	0.1	75.8%	7	7

ISOPRENE	0.3	0.5	0.1	52.5%	5	5
2,5-DIMETHYLHEXANE	0.3	0.6	0.0	76.3%	4	5
2,3-DIMETHYLHEXANE	0.3	0.3	0.1	30.8%	5	5
trans-2-BUTENE	0.3	0.8	0.0	102.6%	5	6
1-BUTENE	0.2	0.5	0.0	67.7%	4	5
cis-2-BUTENE	0.2	0.7	0.0	112.8%	4	5
CYCLOPENTENE	0.2	0.4	0.0	17.0%	2	3
trans-2-HEXENE	0.2	0.4	0.0	17.0%	2	3
3-METHYL-1-BUTENE	0.2	0.4	0.0	100.0%	3	4
1-HEXENE	0.1	0.3	0.0	12.5%	2	3
2-METHYL-1-PENTENE	0.1	0.3	0.0	12.5%	2	3
CUMENE (I-PROPYLBENZENE)	0.1	0.2	0.0	9.4%	2	3
cis-2-HEXENE	0.1	0.2	0.0	8.2%	2	3

The PAMS analysis performed on these samples allows a comparison with similar results obtained from the official PAMS monitoring sites in southeast Wisconsin. The tables below show the total non-methane organic hydrocarbon concentrations and the top ten species from all PAMS sites plus Green Bay. Note that the Green Bay average Total NMOC is significantly higher than that of the other sites. Also note that the results reported for Green Bay are based on only 6 samples, whereas the other sites are summations of the 1995 intensive PAMS season.

Table 45: PAMS Total NMOC Comparison (ppbc)

Total NMOC Comparison	Max	Avg
Milwaukee	600.0	70.7
Woodland Dunes	230.0	25.6
Harrington Beach	83.0	21.5
Green Bay	410.9	181.4

Table 46: Top Ten PAMS Parameters Comparison (ppbc)

Parameter Name	GB	Milwaukee	Rank	Woodland Dunes	Rank	Harrington Beach	Rank
N-HEXANE	32.2	1.5	13	0.3	17	0.4	16
N-BUTANE	13.0	3.1	6	1.6	5	1.5	4
I-PENTANE	8.1	6.7	2	1.9	4	2.4	3
ETHANE	6.1	7.3	1	6.1	1	4.1	1
TOLUENE	6.0	5.3	3	1.5	6	1.4	5
PROPANE	5.7	4.8	4	3.4	2	3.1	2
ACETYLENE	4.9	2.6	9	1	8	1.1	7
ETHYLENE	3.6	3.2	5	1.1	7	1.1	6
XYLENES (m & p)	3.1	2.8	8	0.6	14	0.5	13
n-PENTANE	2.9	2.8	7	0.9	9	1	8
BENZENE	2.6	2	12	0.7	12	0.8	11

The table above compares the top ten PAMS parameters observed at Green Bay with the same parameters from the PAMS sites. The columns labeled "Rank" indicate how these parameters compare with others in the other sites. It should be noted that the hexane values for Green Bay are most likely an artifact from the use of this solvent during PUF sample preparation. The preparation area is actively vented outside, and sampling protocol calls for preparing the VOC samples before the PUF samples to minimize contamination. It appears from the results that enough hexane remains in the area to off-set the values obtained.

Volatile Organic Hydrocarbons, Adsorbent Tube Quality Assurance Parameters

Quality assurance parameters for the adsorbent tubes include duplicates and field blanks with every sample. Table 41 on page 42 indicates occurrences of bad pairs for each reported parameter, and discusses membership values which were used to determine whether the data represented was bad or not.

A total of 1378 sample tube parameters were reported in this series of analysis, along with 689 blank parameters. Of these, 141 pairs of data were determined to be bad (20.4%) and 103 blank parameters were above zero (14.9%). Table 48 on the following page documents the detected parameters in the blank tubes, and indicates the ppbv level calculated on the basis of the average sampling volume (56.5 liters).

In addition to the duplicates and blanks, a pair of spiked carbotrap tubes prepared by Mantech Environmental Technology were analyzed to determine the lab's proficiency with this method. Table 47 below documents the results of these tests. The average percent difference across all parameters for each sample is -13.4% and 17.5%, respectively. These results are well within the $^{+}/_{-}$25% QC goal for analytical accuracy. On a parameter basis, however, only benzene, chloroform, xylene and styrene are within the $^{+}/_{-}$25% QC for both samples. A combination of the bad pairs, the blank contamination, the poor analytical recovery and general sampling difficulties led to the discontinuation of the adsorbent tube method for VOCs and the introduction of the passivated stainless steel canister method.

Table 47: Thermal Desorption Proficiency Sample Results

Parameter	EPA ng	SLOH ng	% Diff	EPA ng	SLOH ng	% Diff	Avg % Di
n-hexane					17	0.0%	
acetone	30		-100.0%	59		-100.0%	-100
TCEa	50	31	-38.0%	101	71	-29.7%	-33
CCl2	50	27	-46.0%	100	110	10.0%	-18
benzene	33	32	-3.0%	66	76	15.2%	6
TCE	6	7	16.7%	11	25	127.3%	72
CCl3	56	42	-25.0%	112	86	-23.2%	-24
TCEe	6	9	50.0%	12	30	150.0%	100
toluene	52	69	32.7%	104	120	15.4%	24
xylene	53	43	-18.9%	106	110	3.8%	-7
styrene	34	33	-2.9%	68	72	5.9%	1

TCEa = Trichloroethane DCB = Dichlorobenzene CCl3 = Chloroform IPA = Isopropyl Alcohol
CCl2 = Methylene Chloride TCEe = Tetrachloroethene TCE = Trichloroethene

Table 48: Volatile Organic Compounds in Blank Samples

PARAMETER	Date	Ng/Tube	ppbv	PARAMETER	Date	Ng/Tube	ppbv
TCEa	10/02/92	<10	0.032	LIMONENE	04/16/92	3	0.010
TCEa	01/20/93	110	0.357	LIMONENE	04/29/92	6	0.019
DCB	06/07/92	17	0.050	LIMONENE	05/12/92	13	0.041
DCB	07/05/92	9	0.026	LIMONENE	06/07/92	9	0.029
DCB	07/16/92	43	0.127	LIMONENE	06/20/92	4	0.013
DCB	07/29/92	16	0.047	LIMONENE	07/05/92	14	0.044
DCB	08/11/92	11	0.032	LIMONENE	07/16/92	46	0.146
DCB	08/24/92	12	0.035	LIMONENE	07/29/92	18	0.057
DCB	09/06/92	12	0.035	LIMONENE	08/11/92	15	0.048
DCB	09/16/92	7	0.021	LIMONENE	08/24/92	8	0.025
DCB	10/02/92	9	0.026	LIMONENE	09/06/92	6	0.019
DCB	10/15/92	17	0.050	LIMONENE	09/16/92	36	0.114
DCB	10/28/92	21	0.062	LIMONENE	10/02/92	9	0.029
DCB	11/10/92	20	0.059	LIMONENE	10/15/92	12	0.038
DCB	01/20/93	1900	5.592	LIMONENE	10/28/92	100	0.318
DCB	04/25/93	<5	0.015	LIMONENE	11/10/92	57	0.181
PINENE	01/03/92	270	0.858	CCl2	01/14/93	12	0.061
PINENE	02/11/92	48	0.152	CCl2	01/20/93	23	0.117
PINENE	03/08/92	10	0.032	HEXANE	10/15/92	<5	0.025
PINENE	03/21/92	16	0.051	HEXANE	12/19/92	22.9	0.115
PINENE	04/03/92	16	0.051	HEXANE	01/14/93	120	0.603
PINENE	04/16/92	38	0.121	HEXANE	01/20/93	480	2.410
PINENE	04/29/92	5	0.016	HEXANE	01/26/93	153	0.768
PINENE	05/12/92	13	0.041	HEXANE	02/09/93	36	0.181
PINENE	06/07/92	250	0.794	HEXANE	02/22/93	82	0.412
PINENE	06/20/92	61	0.194	HEXANE	04/25/93	48	0.241
PINENE	07/05/92	19	0.060	STYRENE	01/14/93	6	0.030
PINENE	07/16/92	63	0.200	STYRENE	01/20/93	7	0.035
PINENE	07/29/92	3	0.010	TCEe	05/25/92	15	0.039
PINENE	09/16/92	79	0.251	TCEe	06/07/92	47	0.123
PINENE	10/02/92	35	0.111	TCEe	06/20/92	35	0.091
PINENE	10/15/92	<5	0.016	TCEe	07/05/92	120	0.313
PINENE	10/28/92	41	0.130	TCEe	07/16/92	19	0.050
PINENE	11/10/92	100	0.318	TCEe	10/28/92	<20	0.052
BENZENE	07/29/92	6	0.033	TCEe	11/10/92	<20	0.052
BENZENE	09/16/92	<10	0.055	TOLUENE	09/16/92	<10	0.047
BUTANOL	07/16/92	2	0.012	TOLUENE	12/19/92	30.5	0.143
BUTANOL	11/10/92	<5	0.029	TOLUENE	01/14/93	87	0.409
CCl3	01/03/92	120	0.435	TOLUENE	01/20/93	100	0.470
CCl3	06/20/92	33	0.120	TOLUENE	01/26/93	142	0.667
CCl3	09/16/92	3	0.011	TOLUENE	02/09/93	40	0.188
CCl3	10/28/92	<10	0.036	TOLUENE	02/22/93	58	0.272
CCl3	11/10/92	<10	0.036	TOLUENE	04/25/93	15	0.070
CUMENE	07/16/92	7	0.025	TCE	10/02/92	<5	0.016
IPA	10/15/92	<2	0.014	XYLENES	07/16/92	3	0.012
IPA	01/20/93	90	0.648	XYLENES	08/24/92	<5	0.020
IPA	01/26/93	816	5.875	XYLENES	09/06/92	<5	0.020
LIMONENE	01/03/92	9	0.029	XYLENES	09/16/92	<5	0.020
LIMONENE	02/11/92	24	0.076	XYLENES	12/19/92	23	0.094
LIMONENE	03/08/92	8	0.025	XYLENES	01/14/93	12	0.049
LIMONENE	03/21/92	8	0.025	XYLENES	01/20/93	48	0.196

LIMONENE	04/03/92	4	0.013				

Volatile Organic Hydrocarbons, Passivated Canister Quality Assurance Parameters

Canister sampling started somewhat sporadically during the second half of 1994. Samples were not being consistently obtained until early 1995. Analysis of field blanks has not been incorporated directly into the sampling scheme. Part of the analysis contract specifies that canisters be cleaned to <20 ppbc total, with individual target compounds present only at less than 0.2 ppb.

Several attempts at duplicates were made during the first year of sampling, however none of these were successful. In all cases, either the sampling apparatus leaked so that both samples were lost, or analysis was not obtained from the samples for other reasons. Installation of a permanent duplicate manifold, usable for either regular or duplicate samples in September of 1995, and improved lines of communication with the laboratory should correct these problems.

INORGANIC PARAMETERS

Total Suspended Particulate and Metals, Data Completeness

Records for collection of TSP and metal samples begin in July 1991 and continue through the present. Project completeness with reference to TSP and metals is documented in the following tables. The first table relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days. Figure 16 on page 49 presents this data graphically.

Table 49: TSP and Metals Sampling Completeness

	Completeness	Valid	Samples	Void	Sampling Days
Overall	84.4%	205	217	12	243
1991	93.3%	28	30	2	30
1992	95.1%	58	60	2	61
1993	80.3%	49	51	2	61
1994	82.0%	50	54	4	61
1995	66.7%	20	22	2	30

The following tables document analytical completeness in terms of results obtained for samples submitted. This evaluation is made only for metals samples, as all samples submitted for TSP results have had results reported. Reasons for analytical incompleteness may include loss of samples in the laboratory, parameters not analyzed for and samples misplaced by the sample operator or in the mail system. Completeness greater than 100% indicates results reported for samples which were voided and yet still analyzed or analysis in duplicate.

Table 50: TSP and Metals Analytical Completeness

	Samples	Arsenic	Completeness	Cadmium	Completeness
Overall	205	198	96.6%	199	97.1%
1991	28	28	100.0%	28	100.0%
1992	58	58	100.0%	58	100.0%
1993	49	40	81.6%	40	81.6%
1994	50	51	102.0%	51	102.0%
1995	20	21	105.0%	22	110.0%
		Chromium		**Lead**	
Overall	205	198	96.6%	198	96.6%
1991	28	28	100.0%	28	100.0%
1992	58	58	100.0%	58	100.0%
1993	49	40	81.6%	40	81.6%
1994	50	51	102.0%	51	102.0%
1995	20	20	100.0%	20	100.0%
		Selenium		**Vanadium**	
Overall	205	198	96.6%	189	92.2%
1991	28	28	100.0%	28	100.0%
1992	58	58	100.0%	58	100.0%
1993	49	40	81.6%	41	83.7%
1994	50	51	102.0%	54	108.0%
1995	20	20	100.0%	8	40.0%

Total Suspended Particulate and Metals, Analytical Results

Results for TSP analysis of all samples are presented in the following table. Values reported are in ug/M^3. Both overall and yearly averages, maxima, minima and %relative standard deviations are shown. It should be noted that TSP concentrations have exceeded 150 ug/M^3 three times at the Green Bay site; twice in 1991 and once in 1993. All of these values were recorded at the Bay Beach site. One of the 1991 values was concurrent with the fire which imay be related to the maximum PAH values mentioned earlier in the report. Results are presented graphically in figure 17 on page 49.

Table 51: Total Suspended Particulate Results, All Samples and Yearly (ug/m^3)

TSP Results	Average	Maximum	Minimum	%RSD	Samples

Overall	44.41	178.30	6.11	65.5%	208
1991	62.72	178.30	6.11	67.8%	28
1992	40.84	136.52	7.24	69.3%	58
1993	36.10	150.94	8.32	65.3%	49
1994	44.45	104.33	11.41	49.3%	52
1995	49.11	114.64	8.21	50.4%	21

Results of metals analysis by parameter are documented in the table below. Each table presents the data of a single parameter, both on an overall and a yearly basis. All results are in ng/m^3 , and represent maximum possible values. Evaluation criteria are average, maximum and minimum reported values, along with percent relative standard deviation. The numbers of samples analyzed and detects are also included, along with the rate of detection. Overall results and detection data is presented graphically in figures 18 and 19 on page 50.

Parameters which have less than a 90% detection rate have a detects only evaluation reported, and all parameters are reported by year in addition to a summation of the entire sampling period. It should be noted that instrument detection limits have improved over the course of this analysis. The effect of this is most dramatic in the cases of arsenic, selenium and vanadium.

Table 52a: Arsenic Results, Overall and Yearly (ng/m^3)

ARSENIC	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	1.775	11.565	0.471	46.0%	198	60	30.3%
1991	1.997	4.239	1.646	28.0%	28	5	17.9%
1992	1.838	2.329	1.558	8.1%	58	7	12.1%
1993	1.745	2.311	1.581	6.4%	40	2	5.0%
1994	1.579	2.530	0.541	31.0%	51	28	54.9%
1995	1.853	11.565	0.471	129.3%	21	18	85.7%
Detects	1.766	11.565	0.471	82.9%	60		

Table 52b: Cadmium Results, Overall and Yearly (ng/m^3)

CADMIUM	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	0.550	4.008	0.105	87.7%	199	193	97.0%
1991	0.738	4.008	0.115	96.6%	28	27	96.4%
1992	0.559	2.719	0.118	80.8%	58	57	98.3%
1993	0.372	0.856	0.105	52.5%	40	37	92.5%
1994	0.603	3.204	0.119	86.4%	51	50	98.0%
1995	0.490	1.450	0.108	67.2%	22	22	100.0%

Table 52c: Chromium Results, Overall and Yearly (ng/m³)

CHROMIUM	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	3.724	17.150	1.581	85.9%	198	170	85.8%
1991	2.151	4.768	1.646	32.9%	28	9	32.1%
1992	3.408	7.902	1.773	39.6%	58	57	98.3%
1993	4.481	17.150	1.581	59.6%	40	37	92.5%
1994	4.084	13.748	1.623	75.8%	51	47	92.2%
1995	4.409	10.751	1.789	51.6%	20	20	100.0%
Detects	4.037	17.150	1.623	59.8%	170		

Table 52d: Lead Results, Overall and Yearly (ng/m³)

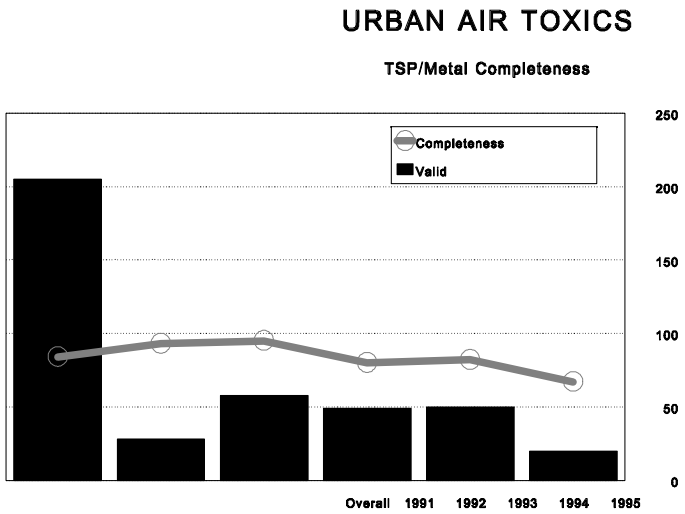
LEAD	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	11.378	81.432	1.581	76.9%	198	192	97.0%
1991	12.982	35.344	3.321	66.3%	28	28	100.0%
1992	9.518	23.752	1.773	64.8%	58	56	96.6%
1993	10.136	33.992	1.581	67.2%	40	37	92.5%
1994	13.121	81.432	1.784	92.7%	51	50	98.0%
1995	12.506	26.571	4.299	54.3%	21	21	100.0%

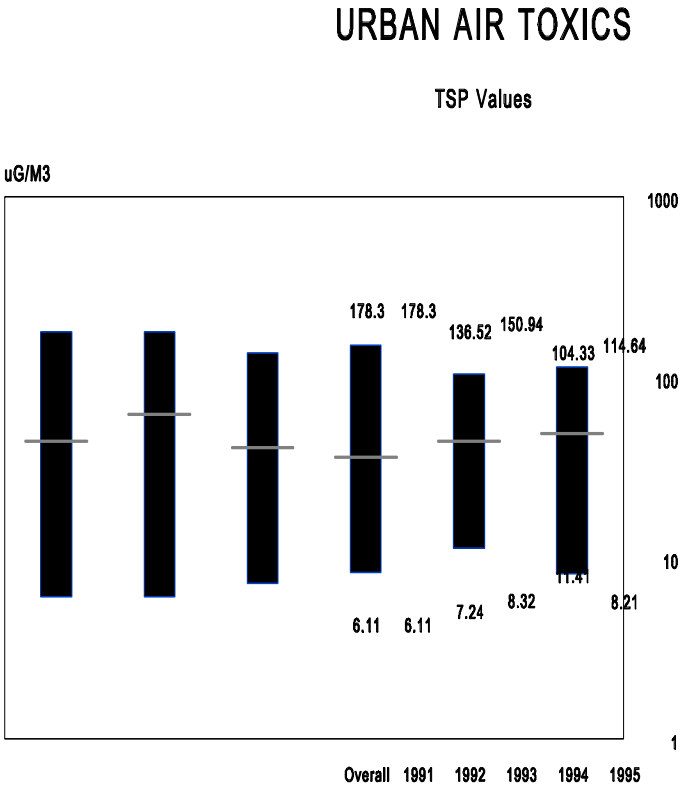
Table 52e: Selenium Results, Overall and Yearly (ng/m³)

SELENIUM	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	1.877	4.505	0.294	32.1%	198	70	35.4 %
1991	1.861	3.854	1.601	22.8%	28	3	10.7%
1992	2.009	4.298	1.558	27.6%	58	13	22.4%
1993	1.891	3.387	1.581	21.6%	40	10	25.0%
1994	1.814	3.830	0.534	35.1%	51	28	54.9%
1995	1.591	4.505	0.294	65.4%	21	16	76.2%
Detects	2.065	4.505	0.294	46.8%	70		

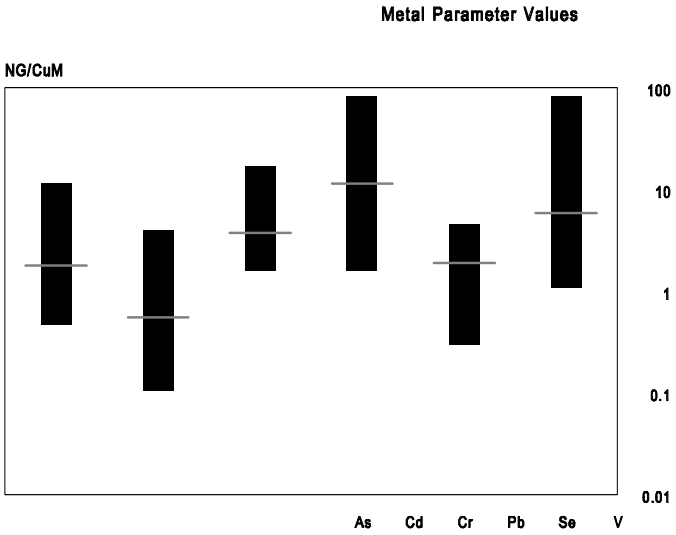
Table 52f: Vanadium Results, Overall and Yearly (ng/m³)

VANADIUM	Average	Maximum	Minimum	%RSD	Samples	Detects	% Detection
Overall	5.281	23.301	1.082	40.3%	183	25	13.7%
1991	5.860	6.150	5.338	3.9%	28	0	0.0%
1992	6.039	7.226	5.195	6.4%	58	0	0.0%
1993	6.209	23.301	5.272	44.2%	40	3	7.5%
1994	3.650	6.417	1.082	61.2%	50	15	30.0%
1995	3.048	6.270	1.084	58.5%	7	7	100.0%
Detects	3.792	23.301	1.084	113.0%	25		


URBAN AIR TOXICS
TSP/Metal Completeness
Completeness
Valid
250
200
150
100
50
0
Overall
1991
1992
1993
1994
1995


URBAN AIR TOXICS
TSP Values
uG/M3
1000
100
10
1
178.3
178.3
136.52
150.94
104.33
114.64
6.11
6.11
7.24
8.32
11.41
8.21
Overall
1991
1992
1993
1994
1995

URBAN AIR TOXICS



Samples were collected from the Bay Beach site between July 1991 and March 1993, and at the Fox River site from April 1993 through the present. Enough data is present to evaluate the sites separately for determining if there is a significant difference between the two sites in terms of metal concentrations. The tables following present the results from each site.

Please note that the maxima for all parameters except cadmium and selenium are significantly higher at Fox River than at Bay Beach. In addition, the chromium average and rate of detection have increased with the move to the Fox River site. This could be a manifestation of locating the site in a parking lot. A graphical representation of yearly chromium data is included as figure 20 on page 54.

Table 53a: Metals Results from Bay Beach

Parameter	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.875	4.239	1.558	18.3%	92	12	13.0%
CADMIUM	0.600	4.008	0.105	17.6%	92	88	95.7%
CHROMIUM	2.953	7.902	1.581	44.0%	92	70	76.1%
LEAD	10.429	35.344	1.581	69.4%	92	88	95.7%
SELENIUM	1.948	4.298	1.558	26.1%	92	18	19.6%
VANADIUM	5.953	7.226	5.195	6.0%	92	0	0.0%
TSP	48.822	178.300	6.110	73.4%	92		

Table 53b: Metals Results from Fox River

Parameter	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.686	11.565	0.471	63.3%	106	48	45.3%
CADMIUM	0.508	3.204	0.108	81.8%	107	105	98.1%
CHROMIUM	4.399	17.150	1.623	64.8%	105	100	95.2%
LEAD	12.201	81.432	1.747	80.4%	106	104	98.1%
SELENIUM	1.812	4.505	0.294	37.0%	106	52	49.1%
VANADIUM	4.603	23.301	1.082	61.7%	91	25	27.5%
TSP	40.908	114.640	8.210	53.2%	116		

In addition to the site and yearly data trend comparisons, enough data is available to perform a seasonal evaluation of both ambient concentrations and detection rates. The data is presented in the tables below. Please note that the chromium and lead maxima occur in winter, at Fox River, and thus may be indicative of vehicle exhaust during winter warm up idling.

Table 54a: TSP and Metals Results by Season: Winter

Parameter	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.779	2.562	1.193	11.9%	40	8	20.0%
CADMIUM	0.648	4.008	0.105	111.7%	40	38	95.0%
CHROMIUM	3.550	17.150	1.581	81.5%	40	33	82.5%
LEAD	11.086	81.432	1.581	116.1%	40	37	92.5%
SELENIUM	1.878	3.704	1.089	23.6%	40	10	25.0%
VANADIUM	5.799	6.609	5.272	4.8%	38	0	0.0%
TSP	41.285	154.060	8.570	77.5%	40		

Table 54b: TSP and Metals Results by Season: Spring

Parameter	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.960	11.565	0.587	79.4%	44	15	34.1%
CADMIUM	0.560	2.013	0.125	68.6%	44	44	100.0%
CHROMIUM	4.044	13.748	1.724	66.1%	43	42	97.7%
LEAD	11.869	31.356	1.848	59.0%	44	43	97.7%
SELENIUM	1.888	4.505	0.587	38.5%	44	15	34.1%
VANADIUM	5.875	6.788	1.216	19.2%	32	4	12.5%
TSP	42.593	136.520	7.240	65.4%	53		

Table 54c: TSP and Metals Results by Season: Summer

Parameter	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.719	3.233	0.471	26.5%	76	26	34.2%
CADMIUM	0.557	3.204	0.116	76.1%	76	74	97.4%
CHROMIUM	3.795	12.847	1.642	56.1%	76	65	85.5%
LEAD	11.040	33.992	1.747	64.1%	76	75	98.7%
SELENIUM	1.919	3.854	0.294	33.1%	76	36	47.4%
VANADIUM	4.764	7.226	1.084	41.1%	76	15	19.7%
TSP	47.403	178.300	7.600	60.4%	78		

Table 54d: TSP and Metals Results by Season: Autumn

Autumn	Average	Maximum	Minimum	%RSD	Samples	Detects	%Detection
ARSENIC	1.686	4.239	0.541	32.0%	38	11	28.9%
CADMIUM	0.434	1.656	0.115	75.7%	38	36	94.7%
CHROMIUM	3.403	8.813	1.623	51.0%	38	30	78.9%
LEAD	11.790	35.344	1.784	69.3%	38	37	97.4%
SELENIUM	1.781	4.298	0.534	29.4%	38	9	23.7%
VANADIUM	5.300	23.301	1.082	65.9%	37	6	16.2%
TSP	44.073	117.530	6.110	63.5%	37		

In addition to the standard suite of metals, a pair of samples were analyzed for an expanded suite of metals using ICAP in an effort to determine whether the parameter list for metals should be expanded. Results of this determination are presented in the following table. Please note that these values are blank corrected, so that negative values indicate a higher blank than sample value. Positive values are presented graphically in figure 21 on page 54.

Table 55: Other Metals in Green Bay Air

Parameter	Sample 1	Sample 2
ALUMINUM	303.67	225.20
BARIUM	12.02	6.09
CALCIUM	11450.80	5538.82
COPPER	58.20	251.99
IRON	468.15	645.18
MAGNESIUM	2252.20	2410.30
MANGANESE	12.46	24.77
POTASSIUM	695.91	304.33
SODIUM	3163.2056	-1825.98
ZINC	38.59	57.21

Total Suspended Particulate and Metals, Quality Assurance Parameters

Two sets of quality assurance data have been generated for the metals samples. These are a single blank sample reported, and 2 EPA proficiency audit samples. Results from these samples are presented in the tables following. Please note that the blank filter was analyzed both by Atomic Absorption (AA) and Ion Coupled Argon Plasma (ICAP), as the determination was made along with a general ICAP screening to determine whether any other parameters of interest

were being detected in Green Bay's air. Ng/m^3 values are based on an average sampling volume of 2000 m^3. The blank sample was obtained on 6/27/95 and prepared for use with the ICAP determination of other metals.

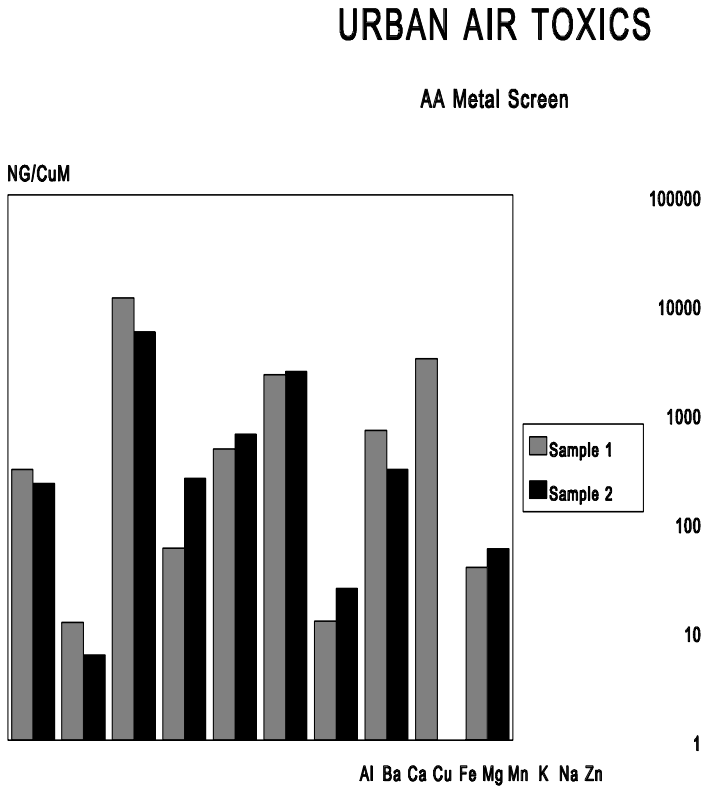

URBAN AIR TOXICS
AA Metal Screen
NG/CuM
100000
10000
1000
100
10
1
Sample 1
Sample 2
Al Ba Ca Cu Fe Mg Mn K Na Zn

Table 56: Metal Parameters in Filter Blanks

Parameter	Analysis	ug/Filter	ng/m^3
Cadmium	AA	0.108	0.054
Chromium	AA	3.6	1.8
Lead	AA	4.8	2.4
Lead	ICAP	15.6	7.8

A pair of EPA round robin proficiency samples were determined by the laboratory, with one reported on 4/13/92, and the other on 2/17/93. Results of the samples and comparisons with the EPA's assigned range and mean are shown in the tables below. Values are in ug per sample. **Bolded** values in the Reported column represent values which fall outside of the 95% confidence interval as determined by US EPA. The ***bold italicized*** value in the % Difference column represent a value exceeding the 25% goal set forth in the HAC QAPP. Please note that the samples come from the same batch, and contain no Vanadium.

Table 57a: Metals Proficiency Sample #L61 (ug)

Parameter	Lower	Upper	Mean	Reported	Difference	% Difference
Arsenic	5.56	7.16	6.36	6.16	0.20	3.1%
Cadmium	6.38	7.62	7.00	**8.85**	1.85	***26.4%***
Chromium	8.87	9.67	9.27	**8.77**	0.50	5.4%
Lead	33.82	43.58	38.70	**45.00**	6.30	16.3%
Selenium	3.71	4.15	3.93	3.72	0.21	5.3%

Table 57b: Metals Proficiency Sample #100LI-7 (ug)

Parameter	Lower	Upper	Mean	Reported	Difference	% Difference
Arsenic	5.56	7.16	6.36	6.53	0.17	2.7%
Cadmium	6.38	7.62	7.00	**7.93**	0.93	13.3%
Chromium	8.87	9.67	9.27	**8.58**	0.69	7.4%
Lead	33.82	43.58	38.70	**43.90**	5.20	13.4%
Selenium	3.71	4.15	3.93	3.91	0.02	0.5%

Metals, Data Comparisons

A significant body of material is available concerning concentrations of various metals in ambient air. Among the most revealing is a comparison of Lead concentrations between the early 1970's and present. Lead levels at that time were found to average 1 - 3 ug/m^3 in urban areas, 0.1 - 0.5 ug/m^3 in suburban areas, and less than 0.05 ug/m^3 in rural areas. Values obtained in Green Bay

average 0.011 ug/m^3 (11 ng/m^3), while a recent nationwide survey of 465 samples yielded an average of 0.009 ug/m^3. This dramatic decrease can be attributed directly to the discontinuation of lead in gasoline.

An examination of the AIRS database for the main metal parameters reported between the years 1990 and 1994 revealed the information documented in the following tables. Table 58 documents the number of states reporting each parameter, the total number of observations included in the database, the maximum values, the number of values greater than the Green Bay maximum, the average, the number of site-years included and the Green Bay average. Lead was not included in this evaluation because of the huge number of lead values present in the AIRS database.

It should be noted that the number of reported values exceeding the Green Bay maximum may be low for each parameter, as the summary available for this data had only the four highest values reported for each site year. Site years with more than four values greater than Green Bay's maximum were indistinguishable from those which had only four values greater. For the purposes of these tables, "site year" refers to a year's data from a single site. No attempt was made at this time to group the data according to site or year. Each site year was treated as a unique entity.

Also please note that the selenium values in the AIRS database appear to be reported at their detection limit, which is substantially higher than ours. This assumption is based on the fact that all of the values for each state are the same between all of the sites.

Table 58: Comparison of Green Bay with EPA AIRS Metal Parameters (ng/m^3)

Parameter	States	Observations	Maximum	> GB Max	Average	Sites	GB Avg
Arsenic	10	20299	5080	117	10.0	26	1.8
Cadmium	34	20976	3900	514	3.0	547	0.6
Chromium	33	17430	589	242	4.2	513	3.7
Selenium	3	6580	100 *	all *	35.0	110	1.9
Vanadium	33	9572	480	152	7.2	304	5.3

Table 59 below compares lead in Green Bay with quarterly values from other sites in Wisconsin, mostly in Milwaukee. The minimum value reported in the AIRS database for this parameter is 0.01 ug/m^3. It is unknown whether this represents the detection limit for these samples. Please note that the average values reported are based on quarterly arithmetic means rather than raw data.

Table 59: Lead Values in Wisconsin (ug/m^3)

Site	Observations	Maximum	Average
Green Bay	198	0.081	0.011
Madison	4	0.02	0.01
Fish Creek	4	0.01	0.01
Milwaukee a	4	0.09	0.06
Milwaukee b	301		
Milwaukee c	294		

Milwaukee a = Great Lakes Research Center
Site 55-079-0024

Milwaukee b = Fire Dept
Site 55-079-0099

Milwaukee c = Monitor Press
Site 55-079-0127

Evaluation

The toxics monitoring prototype site in Green Bay has managed to provide a significant quantity of information regarding a number of toxic compounds present in the air of this city. Trends over the 4 year period can be analyzed, and comparisons made with similar sampling from other locations. Ample opportunity has been available for the evaluation of methods used to collect and analyze trace components of the atmosphere.

Over the monitoring period to date, a number of method changes have been made to improve detection limits and consistency of results. Some of these changes include lengthening the PCB sampling period from 24 to 72 hours, changing the VOC collection technology from adsorbent tubes to passivated stainless steel canisters, and improving the analytical detection limits for PCBs and metals.

In spite of these changes, additional work remains to be done in improving the methods in use and expanding the toxics monitoring program.

Recommendations

Recommendations regarding continued operations and expansion of the toxics monitoring network fall into two basic categories: further refinements of methods, and expanding the network to different localities. Several of these changes are already being implemented as this report nears completion.

Methodology Changes, PAHs

The semi-volatile organic sampling method currently in place uses a PUF plug as the primary adsorbent. There are indications in the literature that the more volatile of these compounds are lost during the long sampling times, and indeed we see very poor agreement between duplicates for these parameters. It is recommended that the sampling media be changed to incorporate a combination PUF plug/XAD resin cartridge for greater retention of light weight polynuclear aromatic hydrocarbons. Evaluation of this change would include co-located sampling using both collection methods and spiked media used for sampling.

Additionally, the parameter list for polynuclear aromatic hydrocarbons could likely use some adjustment. A standard and more comprehensive suite of PAHs is readily available from the lab. This parameter list includes all parameters which have from time to time been mentioned as being present.

Methodology Changes, PCBs

Conversations with Clyde Sweet of Illinois Water Survey have indicated that during the Green Bay PCB mass balancing work performed several years ago, levels of PCB observed in the ambient air ranged from about 0.1 ng/m^3 in winter to around 1.0 ng/m^3 during warmer months. Summer levels during the 72 hour sampling regime generally confirm these results, but the levels during the colder months are below our method detection limits.

As of November 1995, the PCB sampling time for the winter months (November through April) has been increased to 144 hours. This is an attempt to collect enough sample to be able to determine levels during the winter. Results on this are pending, but it appears that the initial spike did not lose an appreciable amount of analyte during the sampling period.

Additionally, some changes to the parameter list have been advocated by Al Spallatto, who performs the analysis. By his recommendations, we should be looking for cis- and trans-Chlordane, cis- and trans- nonachlor and heptachlor epoxide instead of technical Chlordane; and DDE rather than DDT. Hexachlorobenzene should be dropped from the list. Other changes to the parameter list at this time are not called for.

General Site Operations

Currently the toxic site is undergoing a computerization process, whereby a network linked computer will both control the samplers and perform data logging functions. Ideally, this computer will allow for the generation of a nearly paperless site, with field sheets and calibration information available through the network. Estimated time for the installation of this equipment is during April, 1996.

Re-evaluation of the data in the process of preparing this report has reopened the question of whether or not we should sample for phenols at this site again. Returning to the data has shown that numerous detects were obtained following the conversion from a liquid absorbent to a solid adsorbent matrix.

Expanded quality control and assurance measures are necessary for several of the methods. These measures would include blank filters and duplicate filter strips for metals determinations, blank canisters for VOCs, zero audits for VOCs and Carbonyls, and spikes for as many methods as possible.

Expanding the Toxics Monitoring Program

The original intention of the program was for the Green Bay site to serve as a prototype for a network composed of permanent sites in 4 or 5 cities around the state. The air toxics monitoring network is intended to collect data to provide information to be analyzed for potential health effects, trends and atmospheric chemistry. The prototype site in Green Bay has the additional purpose of evaluating various sampling and analytical methodologies.

Our work at Green Bay has shown that we can obtain reliable data for Semivolatile organic hydrocarbons, polar organic compounds, volatile organic compounds and non-volatile metals. This data can be used to determine potential health effects of exposure to the ambient air and to provide a baseline for evaluation of future trends in the concentration of these materials.

The methods used for these parameters are available to be deployed either at full or partial toxic sites. Such sites can be either permanent and fixed with their own power supply, or temporary using portable power and sampling units, as required for meeting requests for information on air quality around the state.

Monitoring these trace elements and compounds in the atmosphere remains an important aspect of understanding the effect industrial culture has on our ecosystem. Comparison of rural and urban sites from around the state will provide clearer information for evaluating potential health effects and contaminant trends in the atmosphere, in addition to imperative information regarding transport and other issues.

As such, there are several options for how to proceed from here with the Toxics Monitoring program, both in Green Bay and beyond. In general, these options all involve some level of continued monitoring in Green Bay, plus the addition of more sites. The spectrum of options ranges from maintaining a full permanent site in Green Bay (optionally moving it to another city) in addition to an aggressive rotational sampling program using existing TSP sites and portable samplers, to a cut back program involving no fixed sites and minimal rotational sampling.

Potential sites could include Milwaukee (Menominee Valley), Superior, Wausau, Eau Claire, Madison, Janesville, La Crosse, Beloit or another of the Fox Valley cities for urban industrial areas. Trout Lake would be an ideal site for a rural area. Specific locations to be used will be worked out with all interested parties.

The Green Bay site now has nearly 5 years of metals data. The data shows that these parameters occur at low and relatively consistent concentrations in the atmosphere. The methodologies are well established. Metals are especially easy to investigate at other sites, as TSP filters from around the state are submitted to the same lab for determinations. It is recommended that analysis of TSP filters for metals be started at 5 other sites on a monthly basis, while cutting back the Green Bay metals to once a month.

VOC data from Green Bay has been affected by several factors, leading to an insufficient level of data from which any sort of trend analysis can be established. The primary factor leading to this state of affairs is the sampling down time during the introduction of stainless steel canisters. It is recommended that VOC sampling and analysis be continued at the current level for at least another year to generate sufficient baseline data for future trends analysis.

Carbonyl sampling and analysis has been consistently successful, with the database now containing 5 years of data. On this basis, a decrease of sampling activity to once per month would be acceptable to maintain our awareness of carbonyl trends in Green Bay.

PCB and pesticide sampling has been difficult. It is only in the last year that enough data has been generated to be confident that we can obtain reliable results. As such, there is not yet enough data to analyze trends of these materials in the urban atmosphere. There are tantalizing hints based on previous studies in the area that the concentration of PCBs is decreasing, but we do not have enough information to be sure of this. On this basis, PCB sampling should continue in Green Bay for at least another year.

Sampling frequency for PCBs can be altered, however. Between March or April and October or November, concentrations of PCB are readily detectable using current technology. During the rest of the year we don't usually see any. On this basis, cutting back to a summer only sampling schedule for PCBs is a viable option, although obtaining one or two cold season samples to verify is advisable.

PAH sampling methodology is still being refined. It is recommended that sampling for this parameter group continue at the current level for at least the next year at Green Bay. This will allow for the verification of sampling methodology for this important group of compounds, and continue the process of providing a clear picture of what concentrations of these materials are present in our urban air.

In addition to the sampling at Green Bay, it is recommended that some level of rotational sampling for parameters other than metals be started with the funds released from the decreased activity at the Fox River site. We have the capability to remotely sample each of the toxic parameters using portable samplers. Use of these samplers at the various TSP sites chosen for metals analysis on a quarterly rotational basis will go a long way to providing information from which we can site the next Toxics Monitoring station.

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